

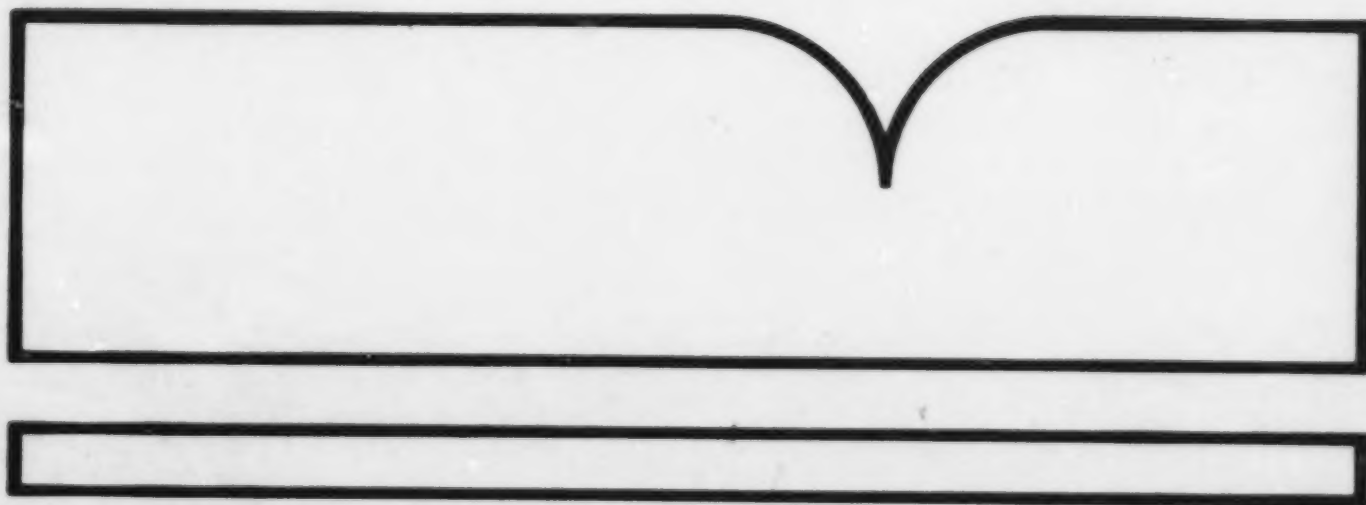
Bench Scale Evaluation of Resins and  
Activated Carbons for Water Purification

Illinois Univ. at Urbana-Champaign

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BENCH SCALE EVALUATION OF RESINS AND ACTIVATED  
CARBONS FOR WATER PURIFICATION

by

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## FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Low but potentially significant concentrations of organic matter in water including known and suspected carcinogens have stimulated the investigation of a variety of adsorbents capable of removing these compounds from water. Part One of this three-part report describes laboratory studies that were used to select adsorbents for use in the pilot plant studies that will be described in Part Two. The overall results will be summarized in Part Three.

Francis T. Mayo, Director  
Municipal Environmental Research  
Laboratory

## ABSTRACT

Adsorption isotherms and bench scale column studies were used to compare the performance of five types of commercially available activated carbon and four types of resin for the removal of humic acids, fulvic acids, 2-methylisoborneol, and chloroform from water. The carbons included two high-activity bituminous carbons (B-1 and B-2), two low-activity bituminous carbons (B-3 and B-4), and a lignite based carbon (L). The resins included weak base phenol formaldehyde resins (R-1a and R-1b), a styrenedivinylbenzene resin (R-2), and a carbonaceous resin (CR).

In the adsorption of humic materials, carbon B-2 performed slightly better than did carbon B-1, while carbon L performed very much like the high-activity carbons. Carbons B-3 and B-4 were inferior to the other carbons. Of the resins, only resins R-1a and R-1b were satisfactory. Adsorption isotherms gave a good indication of the relative adsorption efficiencies of the various carbons and resins in the column tests. Column tests using soil fulvic and leaf fulvic acids also reflected the performance seen in their respective isotherm tests and reinforced the observation that the capacity of a given carbon or resin depends on the source of the organic material it is adsorbing.

In the adsorption of the earthy-musty odor compound 2-methylisoborneol (MIB), carbons B-1 and B-2 again were seen to have the best capacity. The capacity of carbon L was low and on the order of that of carbons B-3 and B-4. The presence of humic acid reduced the capacity of all carbons studied except carbon L. Regeneration of the bench-scale columns of resins CR and R-2 with atmospheric steam and ethanol, both separately and in combination, was not satisfactory. The presence of humic acid had little effect on the capacity of resins R-2 or CR for MIB.

An internal standard method, using 1,1,1-trichloroethane, was employed for the determination of low concentrations of chloroform in water. Little difference in capacity was seen between carbon L or resin CR for chloroform concentrations less than 0.5 mg/l. For the same carbon and resin, little additional effect on capacity was apparent in isotherms performed in the presence of 10 mg/l humic acid.

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## SECTION 1

### INTRODUCTION

#### STATEMENT OF PROBLEM

Widespread publicity by various news media including television, national magazines, and newspapers has recently made the public aware that their drinking water supplies may contain trace amounts of potentially hazardous organic compounds that are not removed by conventional water treatment processes. Surveys such as the National Organics Monitoring Survey (EPA, 1976a) have demonstrated that many different species of organic compounds are present in water supplies and it is now important that alternative procedures for removal of organics be thoroughly examined.

Many studies of the activated carbon adsorption process have been conducted to determine its effectiveness for removal of organic compounds found in water supplies, but comparatively few show the relative effectiveness of commercially available synthetic adsorbents as a possible replacement for activated carbon. The adsorption capacity of activated carbon can be effectively renewed using thermal regeneration, whereas resin regeneration requires the use of steam, aqueous solutions of base or salt, or nonaqueous solvents; however, it is not known whether compounds adsorbed on resins during water treatment can be removed by such means. Comparative studies are thus required to determine the relative effectiveness of resins and activated carbon and to determine whether there is a potential for using resins in place of activated carbon.

In this study various resins were compared with different types and grades of commercially available activated carbon for application in water treatment. It was carried out within the laboratory using small scale tests, and the data obtained during the initial part of the study were used to recommend the types of adsorbents to be tested in a pilot scale test program under the supervision of Dr. J. T. O'Connor at the Kansas City, Missouri water treatment plant.

#### OBJECTIVES

The specific objective of this project was to determine the efficiency of adsorption of different types of organic water contaminants on several promising resins and carbons, and to determine whether the resins could be regenerated by techniques that could be used at a water treatment plant. This screening study was to be conducted to show potential advantages and

disadvantages of each adsorbent, and to determine whether further testing at the pilot plant was warranted. Specific attention was given early in the study to obtaining data that would permit Dr. J. T. O'Connor, of the University of Missouri at Columbia to select the adsorbents to be used in pilot-scale testing at the Kansas City, Missouri water treatment plant.

## PREVIOUS STUDIES WITH RESINS AND ACTIVATED CARBON

### Adsorption on Resins

Examination of available literature on resins provided much useful information for this study. Many different types of synthetic resins have been used which differ both in the matrix used to make up the resin and in the functional groups attached to the matrix. In particular the reviews contained in Kim et al. (1976a) and Hinrichs and Snoeyink (1976) were used extensively.

Some of the more common matrix compositions are given in Figure 1. A few adsorbent resins are made without additional functional groups, such as the styrene-divinylbenzene (SDVB) resin and the phenol-formaldehyde (PF) resin. It is more typical though for resins to have functional groups which make it possible for substances to be taken up by ion exchange or by specific interaction with the functional group. The strong base ion exchange resins, for example, frequently have the quaternary ammonium functional group (Figure 1:A1) whereas the weak base resins generally have an amine functional group (Figure 1:A2). The strong acid and weak acid functional groups can remove substances from water by cation exchange; typical functional groups are the sulfonate group (Figure 1:C1) and the carboxyl group (Figure 1:C2). In addition, the degree of crosslinking between the polymers which constitute the matrix can be varied and thus resins with different pore size distributions can be prepared.

The strong base resins have been used in a number of applications for removing organic compounds. Anderson and Hansen (1955) examined the SDVB based resins with strong base functional groups (Figure 1:M1, A1) and compared them with the performance of weak base functional groups (Figure 1:M1, C1) for the removal of phenol. The hydroxide form of the strong base resins had a higher capacity than did the chloride form of that resin and the acid chloride form of the weak base resin. The strong base resin could not be regenerated as efficiently as the weak base resin, however, with either an alkaline solution or a polar solvent such as methanol (Pollio and Kunin, 1967). Abrams and Lewon (1962) observed that strong base resins in the chloride form (Figure 1:M1, A1) had a higher capacity for alkylbenzenesulfonate (ABS) detergents than did activated carbon. The capacity was similar to that for a weak base resin in the acid form (Figure 1:M2, A2); however, the authors of that paper indicated a preference for the weak base resin because it could be regenerated more easily (Abrams, 1969). Studies by Rebhun and Kaufman (1967) on the removal of chemical oxygen demand (COD) and color from biologically treated municipal effluent indicated that in general strong acid resins and strong base resins could not be regenerated as effectively as weak base resins, but that the capacity of the strong base resin was approximately that of the weak base resin.

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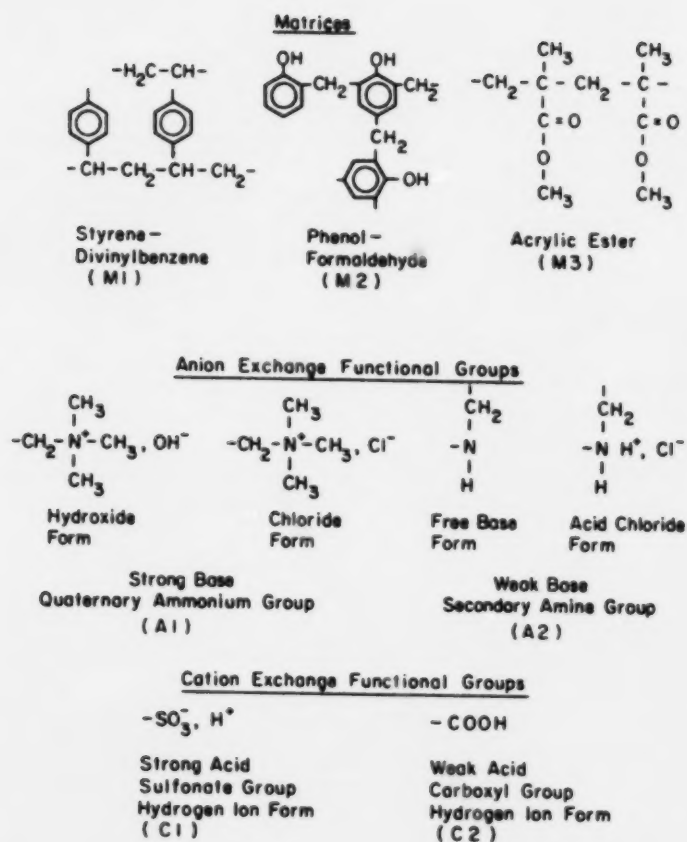


Figure 1. Matrices and functional groups of resins commonly used for water purification after Kim et al., 1976a.

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Kölle (1975) found good removal of total organic carbon (TOC) during ground water treatment at Hanover, West Germany, when a macroporous strong base SDVB resin was used. The resin was regenerated with a NaCl-NaOH solution (100 g/l and 20 g/l, respectively) and the solution could be used several times before disposal. The volume of spent regenerant used could be limited to one unit per 25,000 units of product water which is a very desirable ratio. The tests were carried out in small-scale test systems, however, and plant-scale testing remains to be done. The same resin that Kölle used was used in England to treat Thames River water and resulted in much poorer removals of TOC than that which could be achieved with activated carbon (Gauntlett, 1975). Very frequent regeneration of the resin was found to be necessary as compared to the carbon. Further, the amount of ABS adsorbed during the test and the capacity for trace concentrations of dichlorophenol appeared to be low.

The performance of weak base resins under different conditions of adsorption differs markedly from that of the strong base resins. One of the major differences is the pH dependence of adsorption. Adsorption of phenol on a weak base resin, for example, takes place on the functional group in the free base form (Figure 1:A2). For most weak base resins the free base form predominates at pH 5 and above, and as pH decreases below 5 the amount of functional group in the acid form increases. Acid adsorption by the resin competes with the uptake of phenol, thereby decreasing the amount of phenol that can be adsorbed. As pH increases above approximately 8-9, the OH groups of the phenol-formaldehyde matrix of the weak base resins ionize, and the resulting negatively charged resin will not adsorb negatively charged compounds as well. Also, the phenol itself ionizes and its capacity for adsorption in the ionic form is much less than in the neutral form. Thus, with a phenol-formaldehyde weak base resin, maximum adsorption for phenol occurs near neutral pH and decreases as pH both increases above this range and decreases below this range. On the other hand, ABS is negatively charged and is taken up by the acid form of the resin (Figure 1:A2) by an exchange mechanism. The capacity of weak base resins for ABS is very great at low pH. They do not adsorb to significant degree on the free base form of the resin and thus the capacity near neutral pH is much lower than at a relatively acidic pH.

Weak base resins were also found to have a good capacity for virus and protein relative to a typical activated carbon (Foster et al., 1977) and good results were observed with the use of such a resin for the removal of color from a kraft paper industry waste (Ruzickova, 1970).

An advantage of the weak base resins as compared to the strong base resins is that the former generally can be regenerated more easily. They have a lower affinity for the anionic organics and as a result the organics can be displaced by sodium hydroxide solution or salt solution more easily than for the strong base resins. In one application a weak base resin was used in 60 loading-sodium hydroxide regeneration cycles without any noticeable decrease in capacity (Wolff, 1969). The weak base resins were evaluated by Rebhun and Kaufman (1967) and Schmuck and Kaufman (1970) for the removal of organic matter from the effluent from a secondary treatment plant, and, although these resins were found to have a very good capacity for removing

COD and color and to regenerate rather easily with sodium hydroxide solution, a good general solution to the disposal of spent regenerant was not found.

Strong acid (Figure 1:C1) and weak acid (Figure 1:C2) cation exchangers have found little application for removal of organic materials from water, presumably because most of the organics in water are either negatively charged or neutral.

In recent years the SDVB resins with no functional groups (Figure 1:M1) have received much attention as adsorbents. They have been used in the concentration of organic pesticides and related compounds in raw and finished waters in a study of contamination of water supplies (Junk, et al., 1976). They have been shown to be particularly advantageous for removal of chlorinated pesticides from wastewater (Kennedy, 1973). Regeneration was readily accomplished with acetone or isopropanol and the spent regenerant could be reclaimed for reuse. This resin also adsorbed phenols although the capacity was somewhat less than that for weak base resins (Kumagai and Kaufman, 1968). Similar results were determined for adsorption of ABS. The SDVB resin also does not remove COD or color well from the effluent of a secondary sewage treatment plant (Rebhun and Kaufman, 1967; Schnack and Kaufman, 1970), or TOC from Thames River water (Gauntlett, 1975).

The Water Research Center in England recently evaluated synthetic resins in comparison with activated carbon for application in water treatment plants (Gauntlett, 1975). The tests were done on the organics present in coagulated and filtered Thames River water. After initial screening tests they eliminated the SDVB resins (Figure 1:M1) because of very low capacity, and selected three strong base and one weak base resins for additional detailed testing in columns. The strong base resins were of the SDVB matrix (Figure 1:M1) and the acrylic matrix (Figure 1:M3) while the weak base resin had a SDVB matrix. Some additional testing was done with a weak base resin with a phenol-formaldehyde matrix (Figure 1:M2). The results showed that the carbon removed TOC more effectively than any of the resins, and that the strong base resins performed somewhat better than the weak base resin. The weak base resin was found to be more readily regenerated, although attempts to regenerate with ammonium hydroxide solution, and subsequent recovery of the ammonia for reuse, were not quite as successful as those in which sodium hydroxide solution was used. Activated carbon removed the trace concentrations of the compound  $\gamma$ -BHC very effectively, and the weak base resin removed it nearly as well, but the strong base resin removed very little. The general conclusion of the report was that the synthetic resins which were tested were not as effective as activated carbon when evaluated for removal of TOC or specific contaminants, and that resins would not generally be used instead of activated carbon.

Jayes and Abrams (1968) reported on the results of the application of a phenol-formaldehyde weak base resin (Figure 1:M2, A2) for removing color at the Lawrence, Massachusetts, test facility. Although the material that produces the color at this location was not characterized in detail, it was speculated that it consisted of humic substances or natural decay products. The resin was generally quite effective for removing this material, although at times when the river water was extremely high in color a substantial

amount of leakage through the column occurred. Regeneration was accomplished with sodium hydroxide at the rate of 4 lbs per cu ft. On the basis of this test a resin life in excess of 200 cycles of adsorption-regeneration was estimated.

#### Adsorption of Activated Carbon

The application of activated carbon for removal of organic compounds in water treatment plants has been reviewed on frequent occasions, with one of the more recent reviews being that of McCreary and Snoeyink (1977). Accordingly, the subject is not reviewed further at this time. Of direct importance to this study, however, is the report of Snoeyink et al. (1977) in which the adsorption characteristics of several different types of humic substances were determined, as well as the adsorption characteristics of the earthy-musty odor compounds 2-methylisoborneol and geosmin, the chlorophenols, and selected polynuclear aromatic hydrocarbons. Many of the techniques and materials used in that study were used in the current study. It was found that the adsorbability of the humic substances varied widely depending on their source and molecular weight. The haloform formation potential of the different humic substances also varied widely. A general conclusion was that the performance of a typical activated carbon for removal of the humic substances would depend significantly upon the source of the organic matter. Further, MIB and geosmin were both found to be strongly adsorbed on carbon, but their capacity was reduced somewhat when humic substances were present, indicating competition for adsorption sites. The chlorophenols were also found to be adsorbed very strongly, and the different chlorophenols competed for adsorption sites even at the microgram/liter solution concentration. The polynuclear aromatic hydrocarbons were found to be very strongly adsorbed on carbons and no apparent association was observed between the polynuclear aromatics and the humic substances. Only one activated carbon was used in this study, and one of the major objectives in the current study was to extend it to other carbons and resins.

#### APPROACH TO THE STUDY

Several typical organic contaminants were selected for use, including humic substances from various sources, an earthy-musty odor compound and chloroform. These substances are representative of materials that may require removal from natural waters and thus were logical choices for the screening study. Humic substances produce chloroform when they are chlorinated and, for this reason, there is interest in certain locations in removing them before chlorination. Snoeyink et al. (1977) found that both the tendency to form haloforms and the adsorption properties varied widely for the humic materials used in the current study. The carbons and resins used were obtained from commercial sources and selected on the basis of past experience and review of the literature.

In the original proposal it was indicated that dichlorophenol and polynuclear aromatic hydrocarbons would be used as test compounds. Before testing the polynuclear aromatic hydrocarbons, however, other work was completed which showed that they adsorbed very strongly (Snoeyink et al., 1977). Because the

extent of adsorption was so great there appeared to be little merit in studying their adsorption characteristics further. Also, because of the importance of the presence of low concentrations of chloroform which developed in water, it was decided that chloroform should be substituted for dichlorophenol as a test compound for some of the tests. Work by Zogorski and Faust (1974) also showed that dichlorophenol adsorption on carbon took place much as we found the earthy-musty odor compounds to adsorb, thus making additional work with this compound of less importance.

Small-scale laboratory batch and column tests were used to obtain the desired information on adsorption characteristics. These tests are flexible in their design and operation and as such enabled us to look at a wide variety of conditions in a short period of time.

Approximately 5 months after initiation of the study the results obtained were analyzed and used as a basis for recommending to Dr. J. T. O'Connor which resins and carbons should be tested in detail at the pilot plant portion of the program at Kansas City.

## SECTION 2

### CONCLUSIONS

The general conclusion reached from this study is that resins are not applicable as a general adsorbent at water treatment plants. The primary reason is that they are more selective than activated carbon and do not meet the criterion that an adsorbent be able to remove a wide variety of compounds. There are situations in which resins may perform well, however, and to obtain more information on their strengths and weaknesses, it was recommended (see Section 3) that an activated carbon be tested in parallel with specific resins at the pilot plant.

Specific conclusions are as follows:

1. The macroporous phenol-formaldehyde weak-base resin had a high capacity for humic substances, the trihalomethane precursors. Two resins of this type were investigated and it was felt that the resin with the lower exchange capacity should function better as an adsorbent because it has less tendency to swell when used. Previous studies showed that sodium hydroxide could readily regenerate this type of resin.

The removal of humic substances is very sensitive to pH, however, and our studies at different pH levels showed it is very likely that this resin will function well only at pH values close to neutrality. This also is a disadvantage because pH may vary widely, both at a given plant and from one plant to another.

This resin was not able to remove the earthy-musty odor compound, 2-methylisoborneol (MIB). This is a serious disadvantage because many water treatment plants are plagued with earthy-musty odors and activated carbon generally will remove them.

2. The styrene-divinylbenzene adsorbent resin did not adsorb the trihalomethane precursors. It did have some capacity for the earthy-musty odor compound, MIB, but the capacity was considerably less than that of the high-activity bituminous carbons. Preliminary regeneration studies using steam and ethanol also showed that it may be difficult to remove MIB from this resin after it is adsorbed. While larger-scale studies are necessary to show regeneration efficiency conclusively, there was no indication in this study that this resin should be a serious candidate for use at a water treatment plant.

3. The acrylic adsorbent resin had essentially no capacity for the trihalomethane precursors. It is a relatively polar adsorbent and is not expected to adsorb other trace compounds well either. It does not appear to be of use in a water treatment plant.
4. The carbonaceous resin has an excellent capacity for chloroform, and previous studies showed the chloroform can be removed by steam regeneration. This resin may thus be of use in situations where chloroform and closely related compounds must be removed. This resin did not adsorb trihalomethane precursors.

The earthy-musty odor compound, MIB, did adsorb on this material, although somewhat less than on activated carbon, but neither atmospheric steam nor ethanol did a satisfactory job of removing this compound after adsorption. It thus appears that if the carbonaceous resin is used to remove trihalomethanes, it may be necessary to precede it with another adsorbent to 1) remove the compounds which would otherwise irreversibly adsorb on the resin and which may cause it to gradually lose capacity over time, and 2) remove the trihalomethane precursors, if that is necessary.

5. The high-activity bituminous carbons, B-1 and B-2, and the lignite carbon, L, performed very well for the removal of the humic substances. The efficiency of the low-activity bituminous carbons, B-3 and B-4, was poor in comparison. Removal efficiency was dependent on the source of the humic materials, thus indicating that carbon performance may vary greatly from location to location.

The screening studies were limited by the need to use fresh carbon; in practice, if it is necessary to remove the trihalomethane precursors, it will likely be necessary to thermally regenerate the carbon, thus making the properties of the regenerated carbon an important consideration. Further studies are needed on regenerated carbon.

6. Adsorption of the earthy-musty odor compound, MIB, on carbon was approximately proportional to the surface area of the carbon. Thus, the high-activity bituminous carbons showed the best capacity while the lignite and low-activity bituminous carbons had considerably lower capacity.

For the one humic acid examined, the capacity of three of the bituminous carbons was reduced when the humic acid was present. This was not observed for the lignite carbon.

7. The relative efficiency of removal of humic substances and MIB by small columns of activated carbon could be predicted on the basis of the isotherms for these materials.
8. The chloroform isotherms for the carbonaceous resin and the lignite carbon were nearly the same, and when a humic acid was added to the

test solutions no competition for adsorption sites was observed. The observation that the isotherms were nearly the same was surprising because other data on municipal systems have shown the carbonaceous resin to perform significantly better. A possible explanation is that there are organic compounds in the water supplies of these municipal systems which compete for adsorption sites on carbon, but not on the carbonaceous resin.

### SECTION 3

#### RECOMMENDATIONS

1. Approximately 6 months after initiating this screening study, it was recommended that a high-activity bituminous carbon be tested at the pilot plant side-by-side with a weak base phenol formaldehyde resin followed by the carbonaceous resin. The pilot plant was set up and was operated at the Kansas City, Missouri water treatment plant under the supervision of Professor John T. O'Connor of the University of Missouri.

The high-activity bituminous carbon was selected because of its good capacity for both humic substances and MIB. The lignite carbon had a good capacity for humic substances, but its capacity for MIB was not as good. Of the two high-activity carbons, B-2 was better for humic substances, but B-1 was better for MIB. An arbitrary choice was made and B-1 was recommended for use.

The weak base resin was selected because of its capacity for trihalomethane precursors at near neutral pH. Because this resin will not adsorb MIB (and most likely not chloroform), it was also recommended that the weak base resin be followed with the carbonaceous resin which has a good capacity for chloroform.

The side-by-side testing of the carbon and the resins should give further indication of the relative effectiveness of these materials, and should provide information on regeneration on a large scale.

2. Because of the difference in adsorption effectiveness of the carbons studied for the various humic substances, it is recommended that tests be conducted at each water treatment plant where carbon adsorption is contemplated for the purpose of developing design criteria for the removal of these haloform precursors.
3. While our laboratory studies showed that the humic substances could be removed very effectively by the weak-base resin, subsequent pilot-scale studies at Kansas City showed that the resin was very ineffective. Possibly this is attributable to the high pH (approximately 9-10) of this water and the fact that the weak-base resin performs poorly at high pH. It could also be due to the type of organic matter present. It is recommended that further tests be done with strong-base resins which should perform better at high pH. Further laboratory studies involving the use of strong-base resins have been initiated in our

laboratory and should be complete in the near future. Spent regenerant disposal may be the major problem associated with these materials.

4. In any pilot-scale or large-scale studies involving the carbonaceous resins or other adsorbent resins, and where steam or nonaqueous solvents such as ethanol are used for regeneration, the possibility of incomplete removal of adsorbed compounds from these materials during regeneration should be closely examined. The evidence obtained during our small-scale studies indicated that removals might be incomplete.

## SECTION 4

### EXPERIMENTAL MATERIALS AND METHODS

#### ADSORBENTS

##### Activated Carbons

The activated carbons used in this study were selected to be representative of those currently available on the commercial market. Activated carbons differ primarily in the type of raw material used; in the details of the activated process and in their manufacture. The activated carbons used in this study were manufactured from either bituminous or lignite coal. Some of their properties are shown in Table 1. Some major differences are in the surface area, density, and pore size distribution. Carbons B-1 and B-3 are from one manufacturer, carbons B-2 and B-4 from another, and the lignite carbon, L, from a third manufacturer. Examination of the table shows that as the activity is increased by a manufacturer to make a more active carbon (i.e., higher surface area), the density of the carbon decreases.

TABLE 1. ACTIVATED CARBON PROPERTIES

| Adsorbent | Raw Material    | BET-N <sub>2</sub><br>Surface Area<br>m <sup>2</sup> /g | Bed Density<br>Backwashed and<br>Drained (lbs/ft <sup>3</sup> ) |
|-----------|-----------------|---------------------------------------------------------|-----------------------------------------------------------------|
| B-1       | Bituminous Coal | 1100                                                    | 25.0                                                            |
| B-2       | Bituminous Coal | 1100                                                    | 25.0                                                            |
| B-3       | Bituminous Coal | 900                                                     | 30.0                                                            |
| B-4       | Bituminous Coal | 900                                                     | 30.0                                                            |
| L         | Lignite         | 650                                                     | 23.5                                                            |

The pore size distributions of one particle size of the carbons used in this study, 60 × 80 U.S. Standard Mesh, are given in Figures 2 and 3. These are only representative distributions because the pore size distribution is a function of particle size and probably a function of the way in which the particle size fractions were prepared. Examination of the distributions shows that the high-activity bituminous carbons, B-1 and B-2, generally have more pore volume in all pore-size ranges than do the low-activity bituminous carbons, B-3 and B-4. Carbons B-1 and B-2 are quite similar, except for the somewhat larger pore volume for B-2 in the size range 100 to 5000 Å. It is important to note the major difference between the high-activity bituminous carbons and the lignite carbon. The lignite carbon has many fewer pores with radius <50 Å, but many more pores in the 50-2000 Å range. Because of the small volume of micropores in particular, the total surface area of carbon L is much less than that of carbons B-1 and B-2. An additional major difference is that the lignite carbon has a much higher ash (or inorganic) content than do the bituminous carbons.

The carbons used in this study were prepared by grinding to the desired size range, sieving, exhaustively washing with deionized water to eliminate carbon fines, and drying at approximately 110 °C.

#### Synthetic Resins

Several synthetic resins were selected for testing on the basis of our analysis of the literature and our past experience (c.f., Hinrichs and Snoeyink, 1976; Kim et al., 1976a). These resins are listed in Table 2 along with several of their important properties. Two phenol-formaldehyde resins with amine functional groups were used, resins R-1a and R-1b. The major difference between these is the higher exchange capacity (i.e., higher density of functional groups) and lower degree of cross-linking of R-1a.

TABLE 2. ADSORBENT RESIN PROPERTIES

| Resin | Matrix Composition     | Functional Group | Exchange Capacity meq/g | BET-N <sub>2</sub> Surface Area m <sup>2</sup> /g |
|-------|------------------------|------------------|-------------------------|---------------------------------------------------|
| R-1a  | Phenol-Formaldehyde    | amine            | 9.1                     | ---                                               |
| R-1b  | Phenol-Formaldehyde    | amine            | 2.5                     | ---                                               |
| R-2   | Styrene-Divinylbenzene | none             | ---                     | 300                                               |
| R-3   | Acrylic                | none             | ---                     | 200                                               |
| CR    | Carbonized resin       | ----             | ---                     | 400                                               |

For this reason, resin R-1a is more likely to swell during the adsorption and regeneration processes. The higher headloss and other operational problems caused by the swelling make resin R-1a the less desirable resin of the two even though it had the higher adsorption capacity. These resins were selected for testing because of favorable previous experience (see discussion in Section 1). They were prepared by alternate washing with strong acid, strong base, and methanol as previously described (Kim et al., 1976a).

Resins R-2 and R-3 also were selected on the basis of past experience. Resin R-2 has been extensively used to separate and concentrate trace organics from water (Junk et al., 1974 and 1976) and resin R-3 is especially effective in adsorbing humic materials at very low pH (Snoeyink et al., 1977). These resins were conditioned by washing with methanol followed by Soxhlet extraction with ether, acetonitrile and methanol for 8 hours each, following the method of Junk et al. (1974).

Resin CR is a carbonaceous resin which has the appearance of activated carbon. It has a very high capacity relative to activated carbon for adsorbing chloroform from Philadelphia tap water (Slejko and Neeley, 1976) and similar results have been obtained in Cincinnati (O. T. Love, 1976, personal communication). The adsorbed chloroform could also be removed using steam as the regenerant. This material has the pore size distribution for 20 x 50 U.S. Standard Mesh material shown in Figure 3; this distribution is unique because most of the surface area is concentrated in pores with a radius in the range of 50-200 Å.

#### ADSORBATES

The humic substances used in these studies were a commercial humic acid (Pfaltz and Bauer), humic acid and fulvic acid derived from leaves and soil, and humic substances in water taken from a well in the Civil Engineering Building at the University of Illinois. These materials were prepared and characterized by Snoeyink et al. (1977). All were demonstrated to form chloroform to varying degrees when reacted with chlorine.

Other compounds used were 2-methylisoborneol (MIB) and chloroform. MIB is a causative agent of earthy-musty odor which is derived from actinomycetes and algae. Previous work in our laboratory has involved development of a procedure to synthesize and quantitatively analyze this compound (Wood and Snoeyink, 1977) and the study of adsorption of MIB on activated carbon in the presence of natural organic matter (Herzing et al., 1977). Chloroform can be formed in the process of water treatment during the chlorination step (Rook, 1976, Stevens et al., 1976) and is a suspected human carcinogen; thus there is considerable interest in its removal from drinking water (EPA, 1976b). The existence of methodology required to identify and quantify both MIB (Herzing et al., 1977) and chloroform (Mieure, 1977; Richard and Junk, 1977) was also a major consideration in the selection of these compounds for study.

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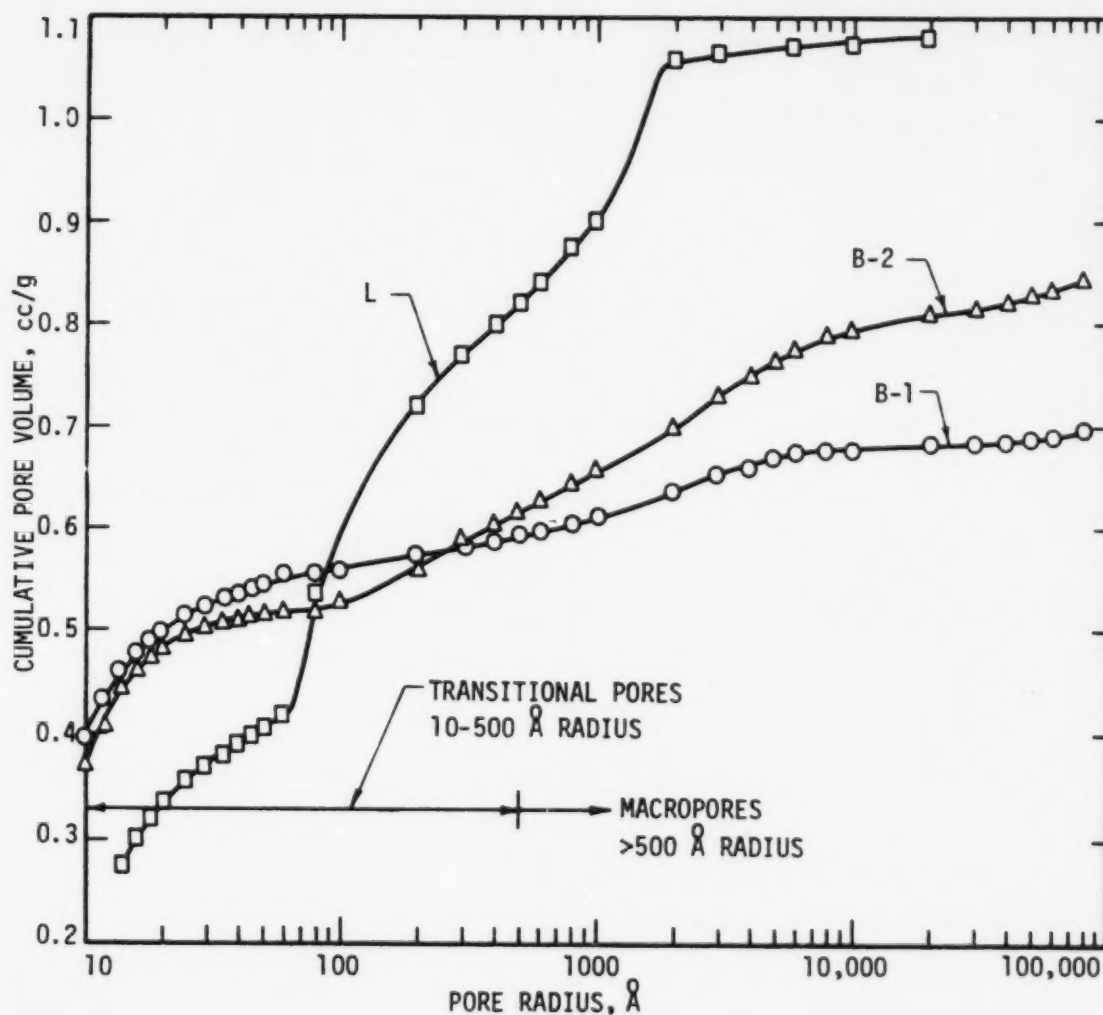


Figure 2. Typical pore size distributions for Carbons B-1, B-2 and L (after Suidan et al., 1978).

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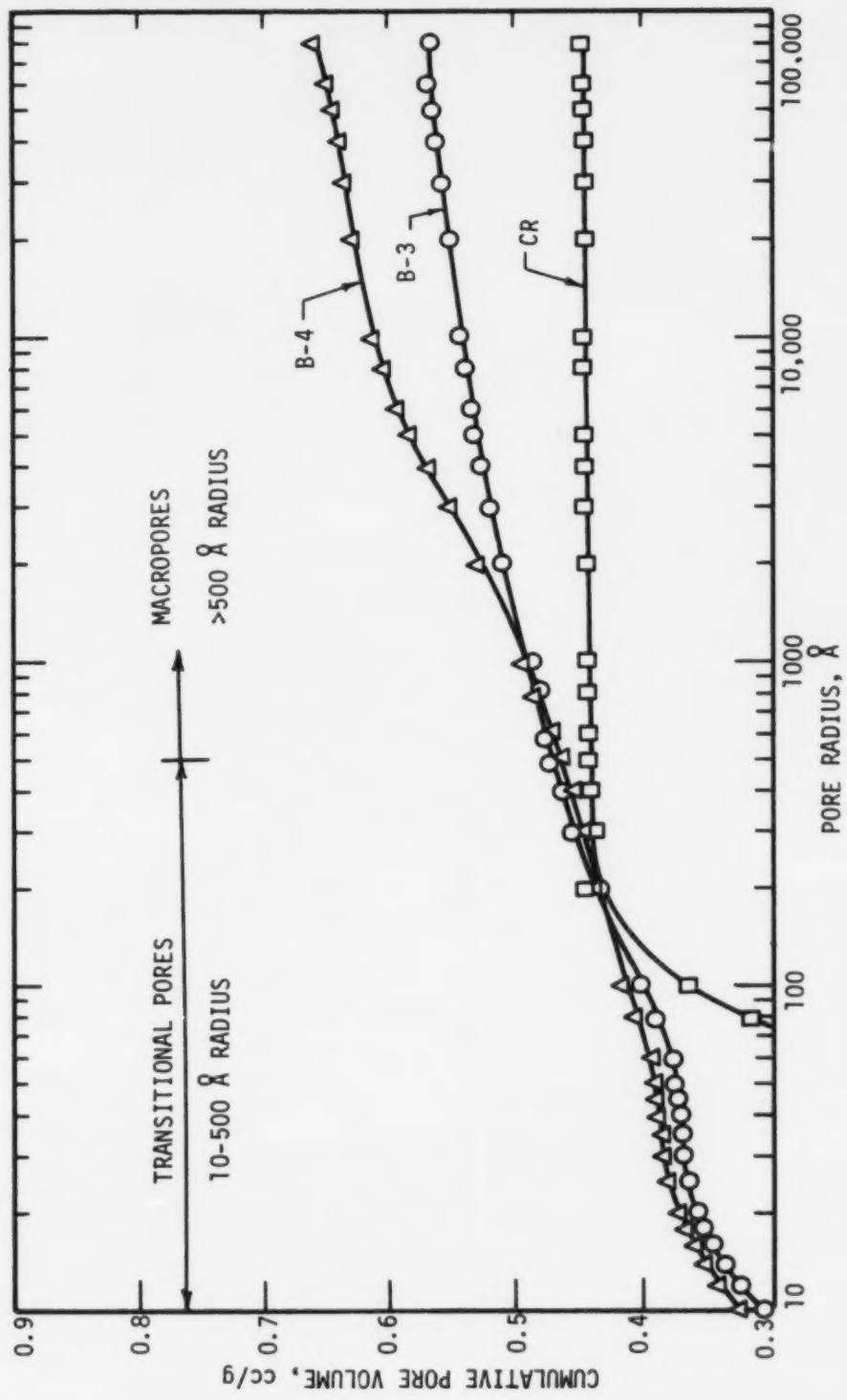


Figure 3. Typical pore size distributions for Carbons B-3 and B-4, and Resin CR (after Suidan et al., 1978).

## SOLUTION PREPARATION AND ANALYTICAL PROCEDURES

MIB was prepared by the method of Wood and Snoeyink (1976). Determination of MIB concentrations in samples was performed by the method of Herzing et al. (1977), which included use of camphor as an internal standard, extraction of aqueous solution with methylene chloride, concentration of the extract, and subsequent analysis via gas chromatography.

Preparation and handling of chloroform solutions required much care to prevent contamination of samples by the trihalomethanes, including chloroform and methylene chloride, which were in use in the laboratory as solvents. All glassware used in handling the solutions was baked 8 hours at 450 °C to remove any trace organics. All water used in making solutions was deionized, glass-distilled, and then purged for 8 hours at 80 °C with zero grade helium or dry grade nitrogen which had been passed through a tube furnace filled with copper-copper oxide catalyst at 900 °C followed by #3A molecular sieves (Linde).

Chloroform solutions were prepared by dissolving 7.0 µl of chloroform (Mallinckrodt Nanograde) in 10.0 ml ethanol (U.S.I. Pure Ethyl Alcohol, U.S.P.) in a 10 ml volumetric flask, resulting in a solution of 1.04 g/l chloroform in ethanol. Two ml of this solution was added to 2.0 l cleaned water resulting in a stock solution of 1040 µg/l chloroform in water which was used in the batch tests. The MIB was also dissolved in ethanol, and the MIB-ethanol solution was then added to the aqueous solutions as described by Herzing et al. (1977).

Standard solutions containing known amounts of chloroform and the internal standard for GC analysis (1,1,1-trichloroethane) were made in the following manner: 8 µl of a solution of 0.593 g/l chloroform in ethanol and 8 µl of a 0.536 g/l 1,1,1-trichloroethane in ethanol solution were added to 20.0 ml of cleaned water in a separatory funnel and shaken vigorously. This yielded a standard solution of 214 µg/l in 1,1,1-trichloroethane and 237 µg/l in chloroform. This standard solution was extracted once with 1.00 ml hexane (Phillips 66 Research Grade Normal Hexane). The resulting hexane solution was injected into a Hewlett-Packard model 5650 gas chromatograph using its electron capture detector. Chromatograms were recorded and analyzed using a Hewlett-Packard model 3380A integrator in the internal standard mode. An example of its output is shown in Figure 4. Column conditions are as follows: a 6 ft × 2 mm i.d. silanized glass column (Supelco) packed with 0.2% SP 1000 in 60/80 Carbowax A (Supelco); the column temperature was 70 °C; injection port and detector temperatures were both 180 °C. The gas flow rate (argon-methane passed through Linde 3A molecular sieves) was 24.0 ml/min as measured by a soap bubble meter attached to the detector exhaust.

Solutions containing humic substances were prepared in a similar manner. Except for the tests with well water, humic substances were weighed to make a solution of the desired initial concentration. This solid was dissolved in a few ml of concentrated NaOH and added to the test solution. The pH was then adjusted to the desired level. The TOC of the initial solution was

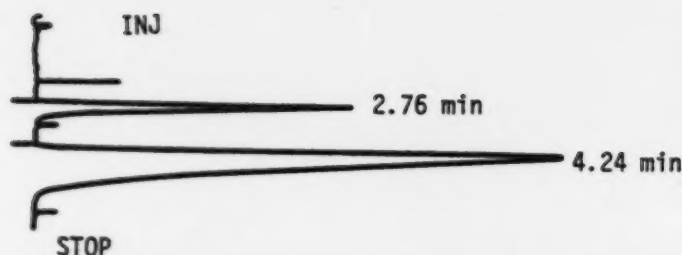


Figure 4. Typical gas chromatogram for chloroform. Hexane extract of a solution of 31  $\mu\text{g/l}$  chloroform (first peak) and 54  $\mu\text{g/l}$  1,1,1-trichloroethane showing the relative retention times and peak areas. Chromatograph attenuation:  $16 \times 10$ ; integrator attenuation: 64.

measured together with the fluorescence of the solution. All measurements after adsorption were made using fluorescence only; the assumption was made that fluorescence intensity was proportional to TOC after Snoeyink et al. (1977). Well water used for the adsorption tests was prepared by aerating and settling to remove iron. The TOC after aeration and settling was approximately 3.5 mg/l.

#### ISOTHERMS AND COLUMN TESTS

Individual isotherm samples were prepared by adding an accurately measured amount of carbon or resin to each of a series of 10 to 15 120-ml bottles. The wet resin which resulted from the cleaning operation was dewatered via centrifuging (5 min @ 5000 rpm, Servall SS-34 centrifuge) in an apparatus designed and built (see below) to facilitate repetitive wet weighing. This allowed the resin to be weighed while at a known moisture content and added to the test solution without difficulty. Rewetting dry resins is frequently difficult and some resins are destroyed when they are heated to dry them.

The apparatus used to dewater resin was constructed as follows: 15 ml coarse sintered-glass funnels were modified by a glass blower so that their overall length was 7.7 cm, 3.2 cm from the frit to the bottom of the tube, which was cut off at right angles to the axis of the tube, and 4.5 cm from the top edge to the frit. Number 5 solid rubber stoppers were bored to form cushions for the glass filters inside  $28 \times 100$  mm stainless steel centrifuge tubes. Resin placed in the top of these modified filters was reproducibly dewatered upon centrifugation. The actual moisture content of separate samples of the resin was obtained by weight difference before and after drying at  $110^\circ\text{C}$  for 8 hours.

For the chloroform isotherms, the carbon or resin-containing bottles were filled to their brims with the stock chloroform solution and sealed with Wheaton aluminum caps with teflon-coated rubber liners. Through careful sealing, air was excluded from the bottles. Upon standing, however, small

bubbles were observed occasionally. The MIB and humic substance isotherms were set up similarly, as described by Herzing et al. (1977), except that no attempt was made to exclude headspace.

The sample bottles were placed on a rotary shaker which provided excellent mixing at a rotation speed of about 25 rpm. Regular complete inversion of the sample bottles provided complete dispersion of the carbon or resin particles in the chloroform solution. The bottles were left on this shaker for at least seven days unless otherwise stated.

The column tests were conducted using 1.3 cm diameter columns containing 2.5-8 cm of adsorbent of uniform size. The solution was applied at a constant flow rate of 6.5 gpm/ft<sup>2</sup> using an Isco model 310 metering pump. The column effluent was analyzed with time to establish the breakthrough curve. Similar tests were conducted by Herzing et al. (1977) using MIB.

The columns of resins R-2 and CR were regenerated using atmospheric steam and ethanol. The steam was produced by a pressure cooker; about 200 ml (condensed basis) was produced per hour. The glass adsorption column was heated using heating tape to prevent excessive condensation of the steam in the column. After passing through the bed, the steam was condensed and the condensate analyzed with respect to time to establish rate and extent of regeneration. The rate of application of ethanol was 250 ml/hour when used for regeneration. The steam and ethanol were applied in the reverse direction of the aqueous solution of organics.

## SECTION 5

### RESULTS AND DISCUSSION

#### ADSORPTION OF HUMIC SUBSTANCES

##### Adsorption Isotherms

Adsorption isotherms were determined for commercial humic acid using several of the adsorbents. This material has a strong tendency to form haloforms when chlorinated and its adsorption characteristics on a single high-activity bituminous carbon were previously reported (Snoeyink et al., 1977). Figure 5 shows isotherms for resins R-1A, R-2 and CR, and carbons B-1, B-2 and L. The resin R-1a, the weak base phenol-formaldehyde resin, had an excellent capacity for this material. The capacity of the lignite carbon L and the bituminous carbons B-2 and B-1 is slightly less than that for the weak base resin. The styrene-divinylbenzene resin R-2 and the carbonaceous resin CR adsorbed insignificant amounts of the humic substance, and thus they do not appear to be useful for removal of this type of trihalomethane precursor.

In Figure 5, the particle size for carbon B-2 is  $40 \times 50$  U.S. Standard mesh while that of the lignite carbon and the carbon B-1 is  $100 \times 200$  mesh. It is possible that this particle size variation makes a small change in capacity, but separate studies on carbon B-2 in which the  $40 \times 50$  particle size was compared with the  $100 \times 200$  particle size showed an insignificant change in capacity. It is thus assumed for this study that while some change in capacity for humic substances may result from this particle size variation, it will not be a major change. The reason the smaller particle size was used to improve the efficiency of mixing of the carbon with the solution during agitation; all of the isotherms determined in the latter part of the study were done with the smaller particle size. The resins were not ground as the carbons were, but for resins R-1a and R-2, the  $40 \times 60$  mesh fraction was screened out of the mixture of particle sizes commercially supplied and used. The carbonaceous resin, CR, was used as supplied by the manufacturer.

When adsorption isotherms are determined for a heterogeneous mix of compounds, such as is the case with the humic acid, the position of the adsorption isotherm may be determined by the initial concentration of the isotherm test solution. To test this possibility, isotherms were determined for carbon B-2 using several different initial concentrations. The results showed essentially no difference in the position of the isotherm.

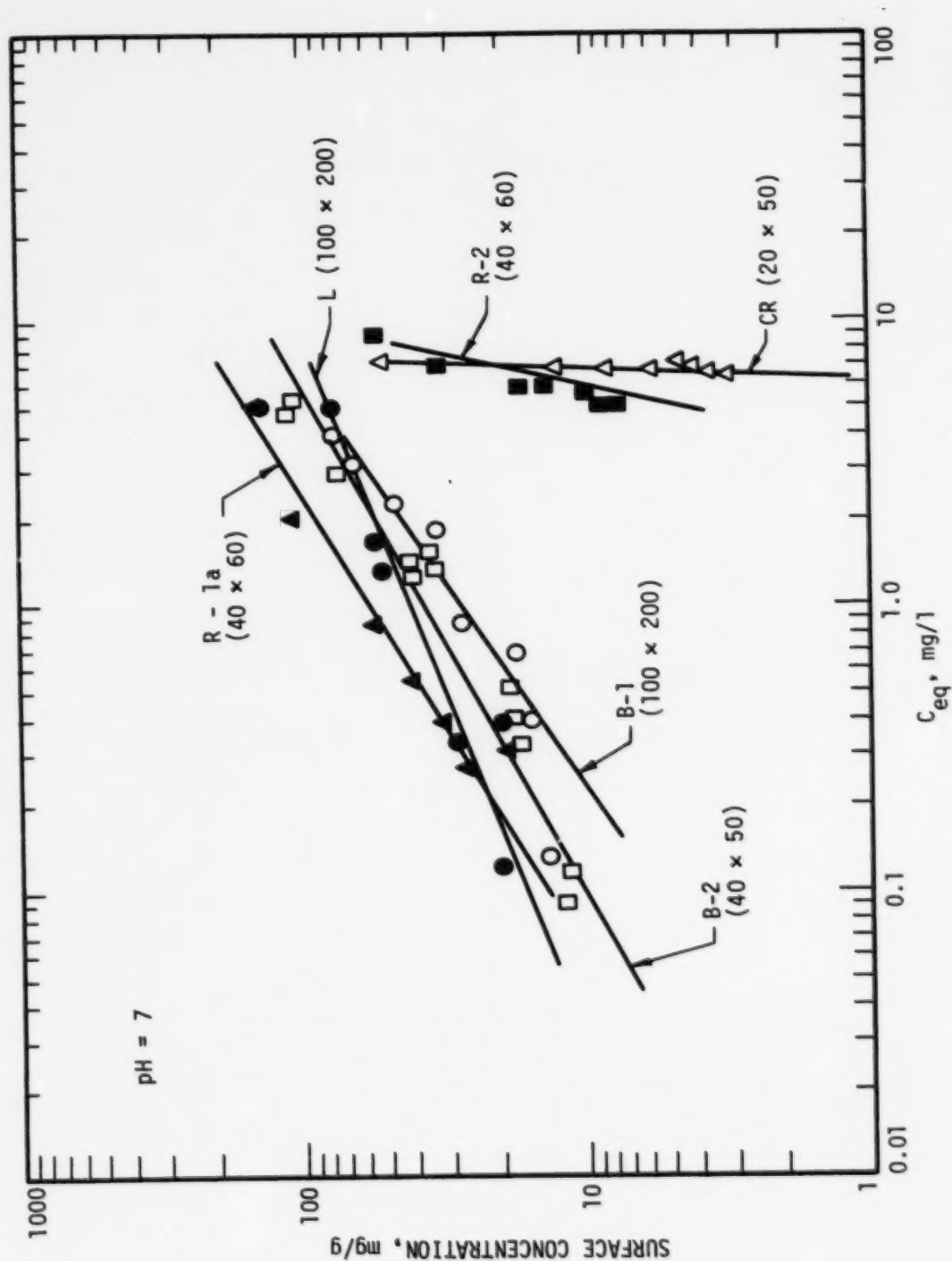


Figure 5. Commercial humic acid isotherms for Resins R-1a, R-2 and CR, and Carbons B-1, B-2 and L.

The results of adsorption of this commercial humic acid on the carbon is interesting when one examines them in light of the pore size distributions. Carbon L, as shown in Table 1, has a surface area of  $650 \text{ m}^2/\text{g}$ , while carbons B-1 and B-2 have surface areas in excess of  $1000 \text{ m}^2/\text{g}$ , much of which is in pores of radius  $<10 \text{ \AA}$ . However, as shown in Figure 2, much of the surface area in carbon L is available in larger pores. Because the capacity of carbon L for humic acid is equal to or better than that for B-2 and B-1, it appears that the smaller pores in the high activity bituminous carbons are not generally available to the molecules which make up commercial humic acid. Because the size of molecules causing trihalomethane formation when water is chlorinated can vary widely from water source to water source, the specific nature of the material to be adsorbed is especially important in the selection of a carbon for use with a given water source.

Further studies with the commercial humic acid are shown in Figure 6. The performance of resin R-1b, a phenol-formaldehyde weak base resin, and resin R-3, an acrylic base resin, is shown in this figure. Resin R-1b has a smaller number of amine functional groups than does resin R-1a. It also has a higher degree of cross-linking so that it does not swell as much when used. The capacity of resin R-1b is lower than that of resin R-1a by about a factor of 2 at an equilibrium concentration of about  $1 \text{ mg/l}$ , undoubtedly because of its lower exchange capacity. Its capacity is comparable to that of carbon B1.

It was noted in Section 1 that the adsorption capacity of the phenol-formaldehyde resins was dependent upon pH. Figure 6 shows that when the pH is either decreased from 7 to 5.5 or is increased from 7 to 8.3, the capacity drops off significantly. At lowered pH, the amine functional groups adsorb acid thus reducing the amount of organic material which can be adsorbed at those sites. As the pH is increased from 7, and particularly above pH 8.3, the OH functional groups on the resin matrix begin to ionize, thus giving the resin a significant negative charge. Because of the negative charge on humic acid, which increases as pH is increased, adsorption capacity on the negatively charged resin is low. Thus, in spite of its high capacity at the natural pH, this resin should not be used in situations where the pH is likely to become very high. Not only do materials not adsorb well, but previously adsorbed material may be desorbed from this resin with a sudden increase in pH.

The resin R-3 has previously been found to adsorb humic substances very well when the solution tested had a pH of around 2 to 3 (Snoeyink et al., 1977). On the basis of our past findings, we decided to examine the resin at pH levels of 5.5, 7, and 8. At these pH values, the resin was very ineffective, and accordingly it is not likely to serve satisfactorily in a water treatment plant.

In Figure 7 isotherms are shown for a low-activity and high-activity bituminous carbon, carbons B-4 and B-2, respectively. The low-activity carbon has not only a smaller surface area but also many fewer pores in the size range likely to be effective for adsorbing a humic acid. Thus, the difference in adsorption capacity, shown to be nearly an order of magnitude at an equilibrium concentration of  $1 \text{ mg/l}$ , is not unexpected. Similar results were

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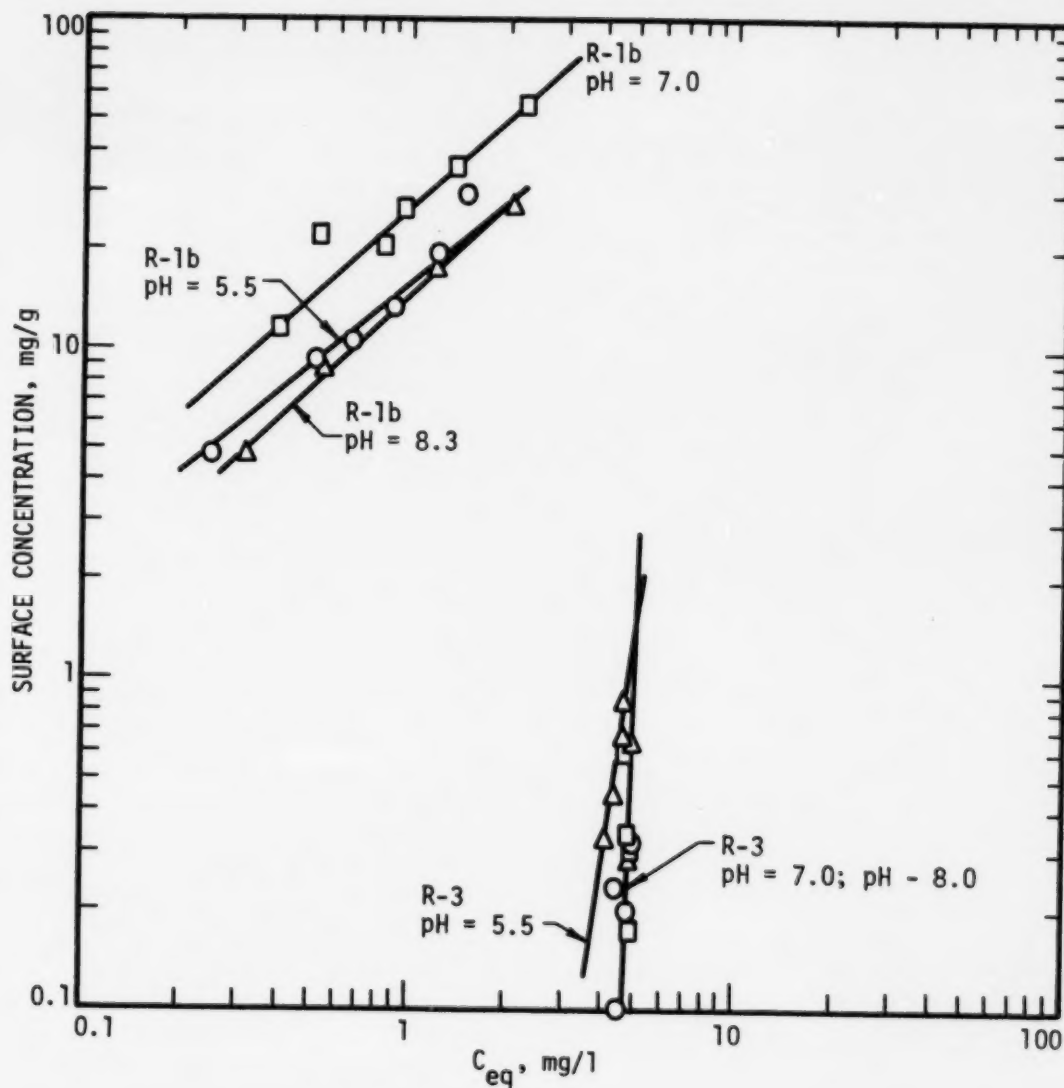


Figure 6. Commercial humic acid isotherms for Resins R-1b and R-3.

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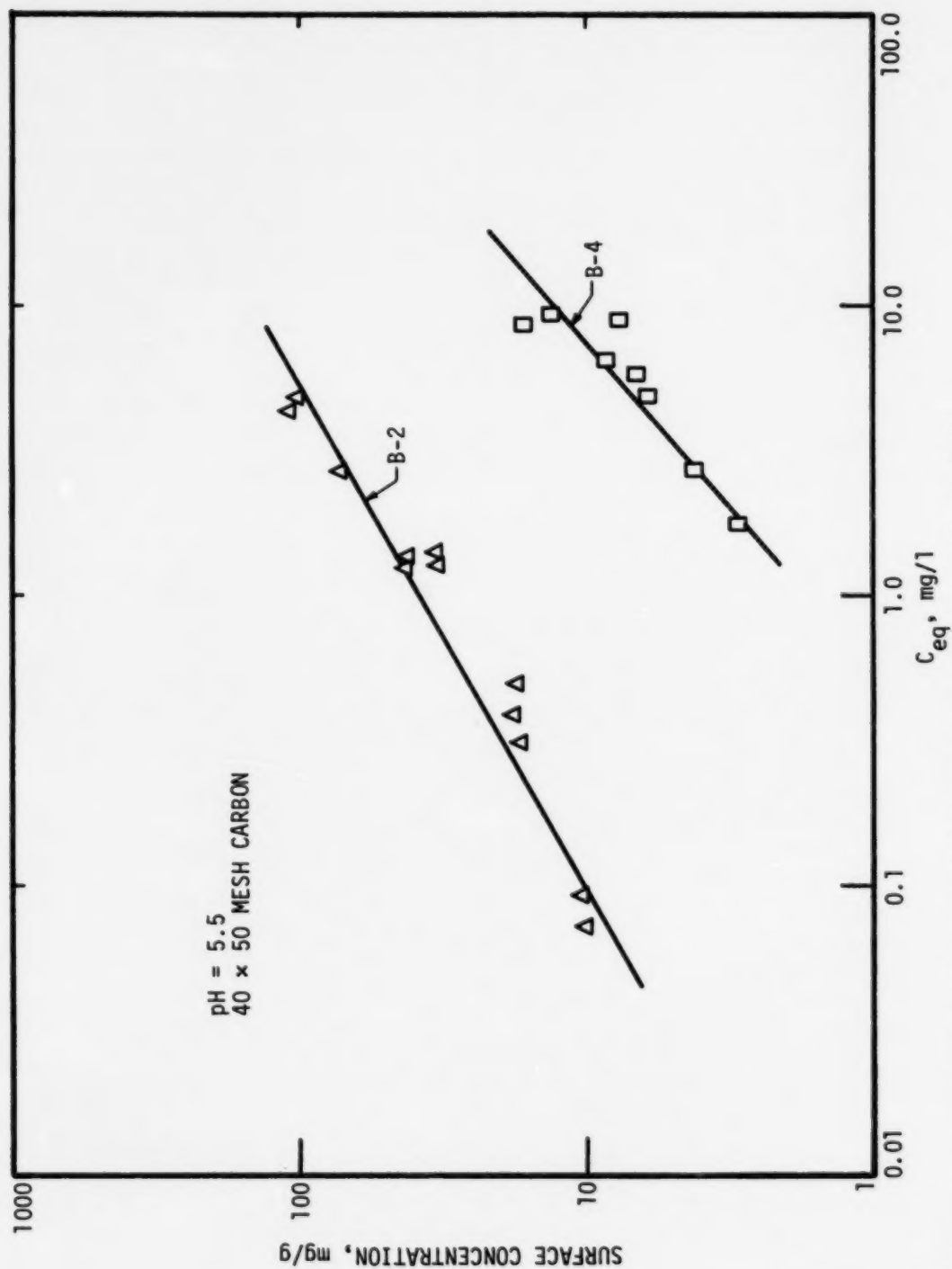


Figure 7. Commercial humic acid isotherms for Carbons B-2 and B-4.

found for these two carbons when isotherms were determined using well water which contained a significant amount of humic substances obtained from a deep well in the Civil Engineering Department Building.

Figures 8, 9, and 10 are adsorption isotherms for soil humic acid, soil fulvic acid, and leaf fulvic acid for carbons B-1, B-2, and L. In these isotherm determinations the phosphate concentration was kept constant. The preparation procedure for these different humic materials involved the use of phosphate salts and because it was not possible to completely separate the phosphate from the organics, some phosphate was present with the fulvic and humic materials.

Sufficient additional phosphate to make the solution  $10^{-3}$  molar in  $\text{PO}_4^{3-}$  was added because Snoeyink et al. (1977) previously showed that the level of phosphate was important. For the soil humic acid, the isotherms for carbons B-1 and B-2 were essentially the same as for the commercial humic acid, with B-2 having the higher capacity. However, the capacity of carbon L was slightly lower than that for B-2. The soil fulvic acid was not as strongly adsorbed as was the soil humic acid. Fulvic acid generally has a lower molecular weight and higher oxygen content than humic acid. It was expected that the high-activity bituminous carbon would perform better than the lignite carbon for this lower molecular weight material since more smaller pores in the high activity carbon should be available for adsorption. The observed effect was not as great as expected, however. One explanation is that a large proportion of the adsorption was still taking place in pores larger than approximately 50 Å radius because carbon L has many more of these. The adsorption isotherms for the leaf fulvic acid for carbons B-1, B-2 and L are, again, very close together. The leaf fulvic acid adsorption isotherms can be seen to be somewhat higher than those for the soil fulvic acid, indicating the importance of the source of the material. While little significant difference is noted among carbons B-1, B-2, and L for the leaf, soil and commercial humic substances, there is a significant difference between the high-activity carbons and the low-activity carbon B-4, as shown by the leaf fulvic acid curves in Figure 10; again this is expected because of the much lower number of pores in the right size range for carbon B-4.

Other work in our laboratory, not presented here, with carbons B-2 and B-4 shows that for both of these carbons the organic matter in well water adsorbed more efficiently by approximately a factor of two on these carbons than did the commercial humic acid.

The effect of pH on adsorption of humic substances was also examined. Figure 11, for example, shows the effect of pH on adsorption of humic material from well water. A significant difference is noted between the adsorption capacities at pH 7 and pH 3.1, with the material absorbing much more strongly at a pH of 3.1. Little difference, however, was noted between the isotherms at pH 7.0 and pH 10.8. By comparison, in studies with the commercial humic acid with the same carbon B-2, essentially no difference was noted between adsorption at pH 7 and pH 3.1. In the case of the commercial humic acid a significant difference was noted between the isotherms at pH 7 and pH 10.8. Other studies with commercial humic acid showed no difference between pH 7 and pH 5.5. Snoeyink et al. (1977) showed significantly different isotherms

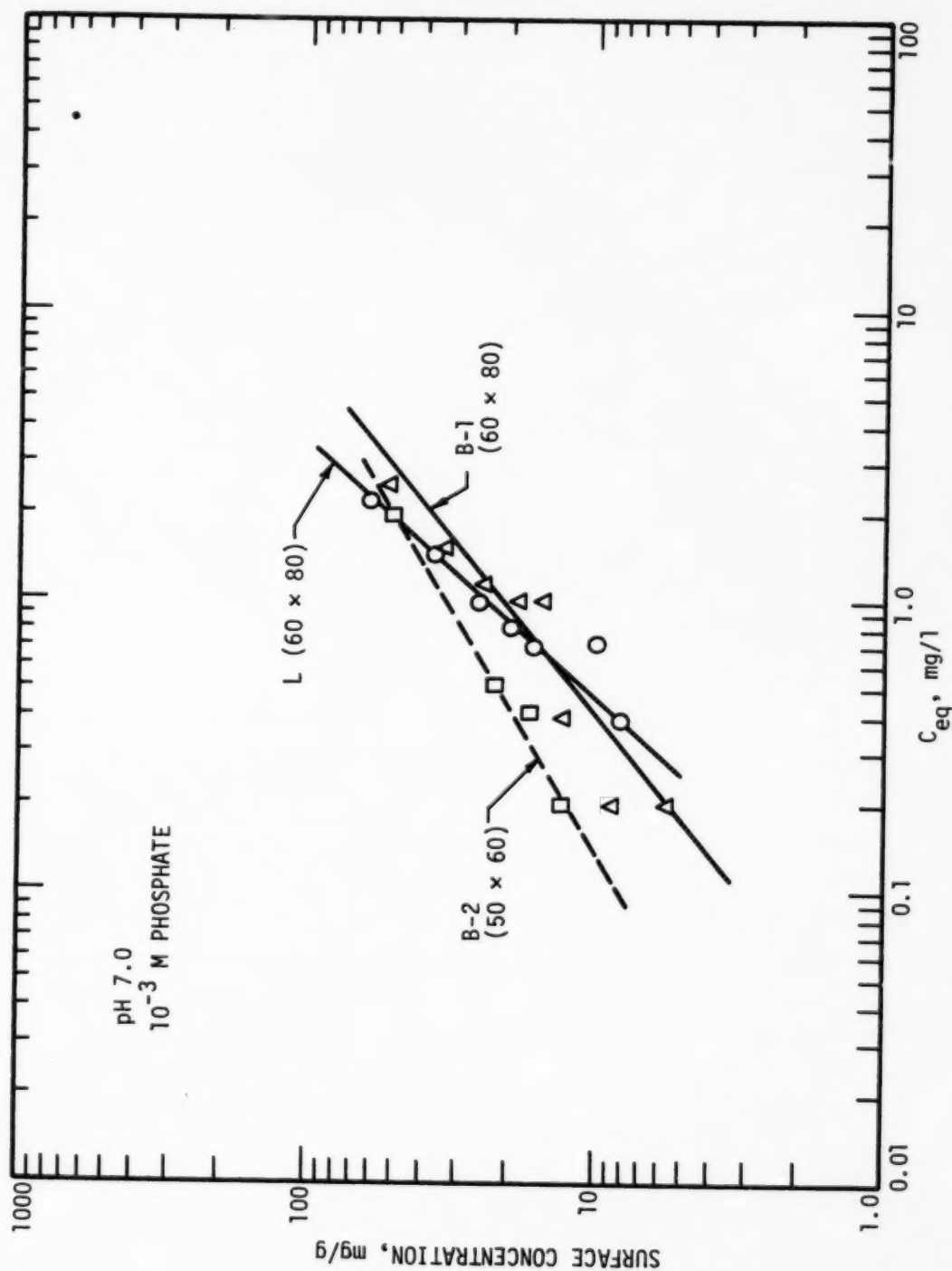


Figure 8. Soil humic acid isotherms for Carbons L, B-1 and B-2.

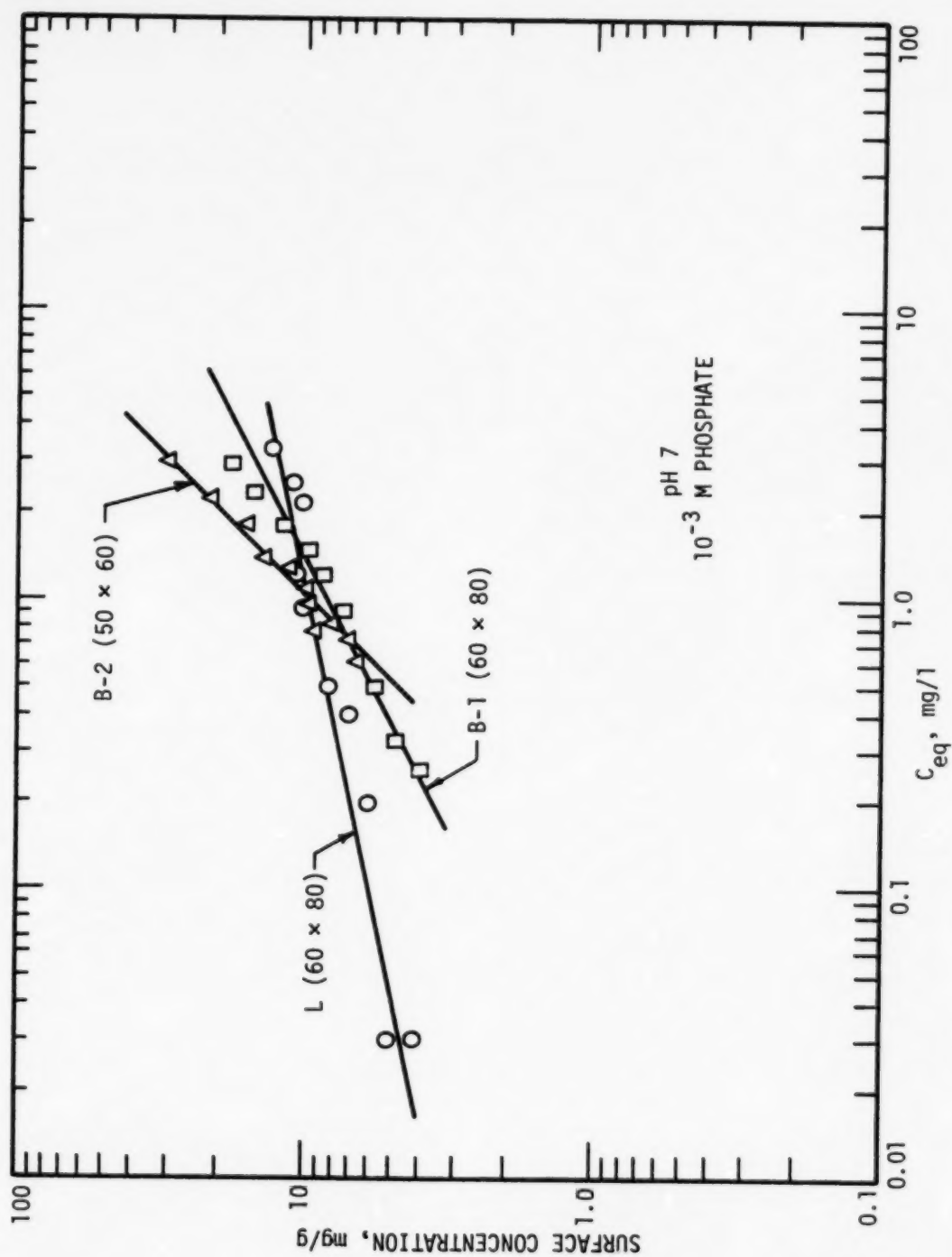


Figure 9. Soil fulvic acid isotherms for Carbons L, B-1, and B-2.

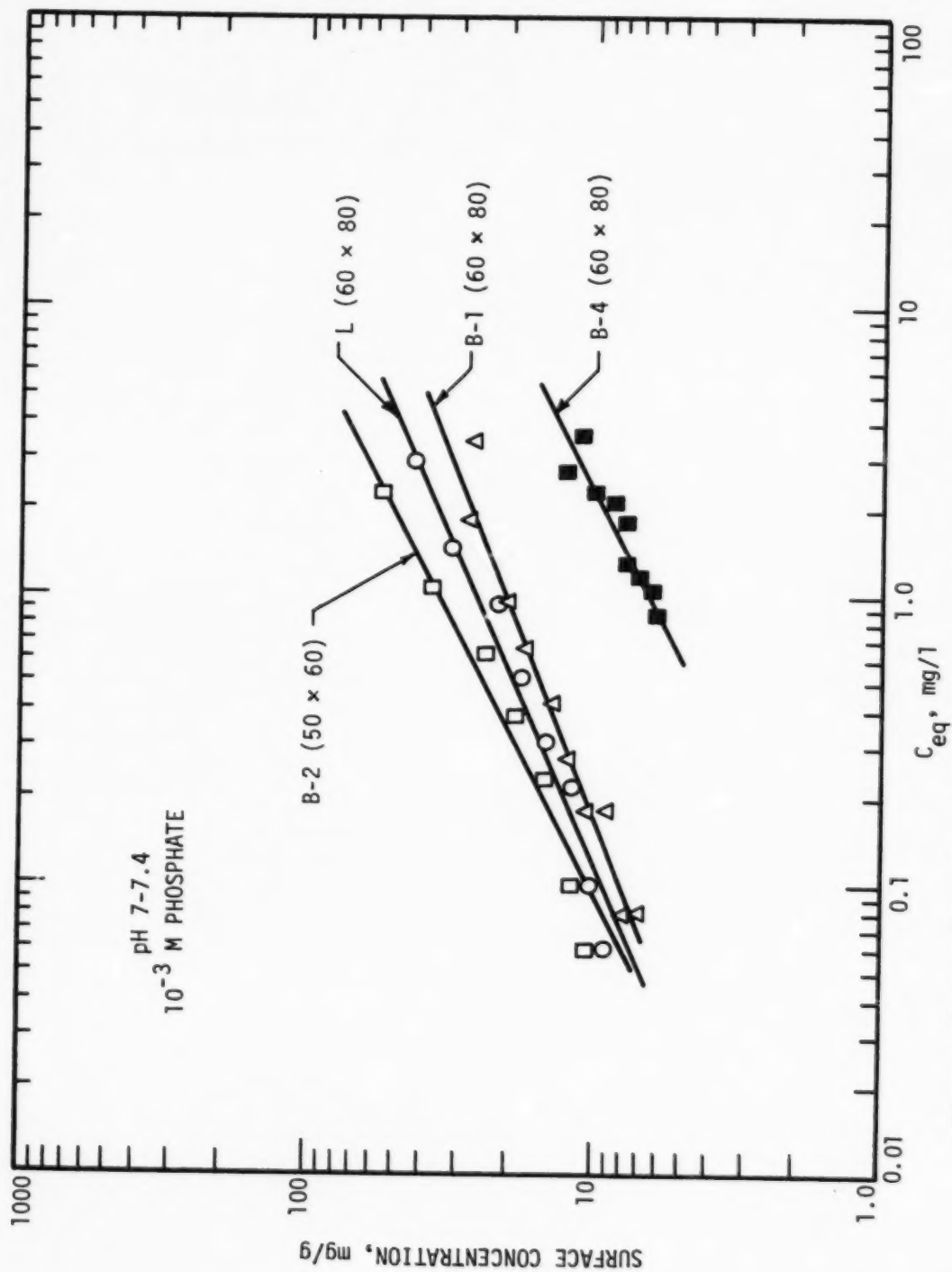


Figure 10. Leaf fulvic acid isotherms for Carbons L, B-1, B-2 and B-4.

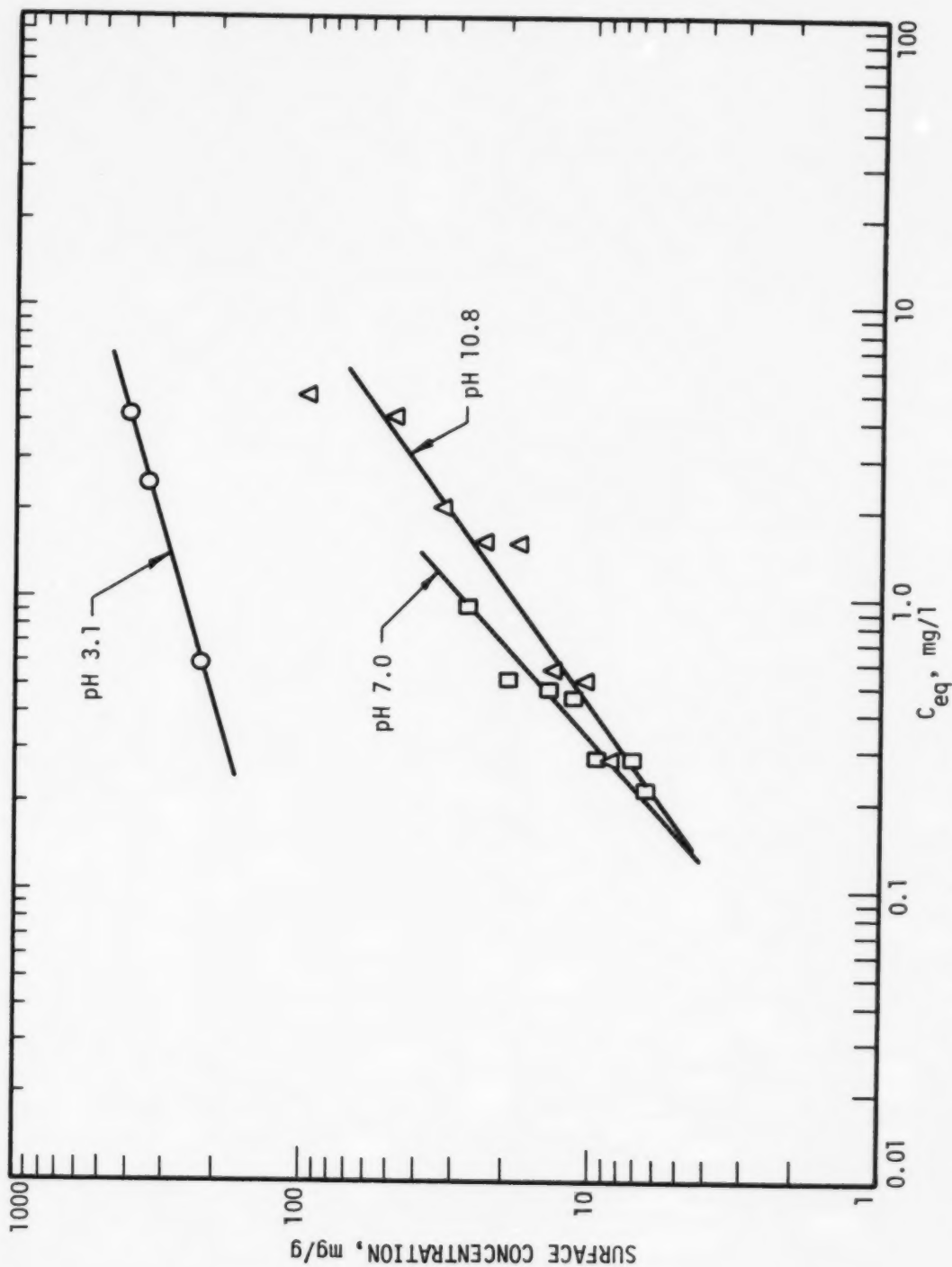


Figure 11. The effect of pH on adsorption of humic acid from well water by Carbon B-2.

for soil fulvic acid at pH values of 11, 8.7, 7, 5.4 and 3.0. The general conclusion from these studies is that it is difficult to predict in advance just what the nature of the pH effect will be, because this effect is dependent upon the source of the material.

#### Column Adsorption Tests

Column adsorption tests were conducted to determine whether the relative effectiveness of the carbons as predicted from the isotherms were indeed what would be observed in the columns. The columns were bench scale, generally containing 2 grams of carbon in a 1.3 cm diameter column with a resulting column length of approximately 3.8 cm. A flow rate of 6.5 gpm/ft<sup>2</sup> was used. It should be emphasized that the test was not to determine what effluent quality can be achieved over a period of time in large scale installations, since this information is best derived from larger scale columns such as would be conducted at a pilot plant. Typical results for commercial humic acid are shown in Figure 12 for carbons B-1 and B-2. On the basis of the isotherms shown in Figure 5, carbon B-2 should have a better capacity than carbon B-1. An analysis of Figure 12 shows that carbon B-2 has indeed adsorbed more material than B-1 during the column run of approximately 20 hours. Beginning at about 8 to 10 hours, and continuing thereafter, the rate of saturation of the carbon was very slow, presumably because of the time required for the large molecules to penetrate into small pores in the carbon. The general conclusion to be drawn from Figure 12 is that the relative adsorption effectiveness as indicated by Figure 5 holds when the carbon is applied in a column. In order to achieve better effluent quality, a lower rate of application could be used together with much deeper beds of carbon. Studies of these parameters are necessary to predict the actual life of larger beds of carbon.

Figure 13 shows breakthrough curves for commercial humic acid adsorption on carbons L and B-4. An analysis of Figures 5 and 6 would result in the prediction that carbon L should adsorb much more in a column than carbon B-4, as was observed. Duplicate runs have shown the same information.

Column runs for adsorption of leaf fulvic acid on carbons B-1, B-2, B-4, and L are compared in Figure 14. From Figure 10 we expected that the capacity of carbon B-4 would be much lower than that of the other three carbons, but that for the other three carbons the sequence should have been B-2 > L > B-1. What we found was that L and B-2 had essentially the same capacity and B-1 had slightly less capacity. Thus, the column runs did not show quite as much difference between the carbons as did the isotherm tests. This gives us some idea as to the degree of significance that should be placed on the differences noted in the isotherm tests. The soil fulvic acid results in Figure 15 lead to essentially the same conclusions as those which were observed for the leaf fulvic acid.

The general conclusions to be drawn from our studies of adsorption of humic substances are that, of the high-activity bituminous carbons, carbon B-2 performs slightly better than carbon B-1 and that the lignite carbon has a capacity very close to that of the two high-activity bituminous carbons. Of course, all of our experiments were done using fresh carbon,

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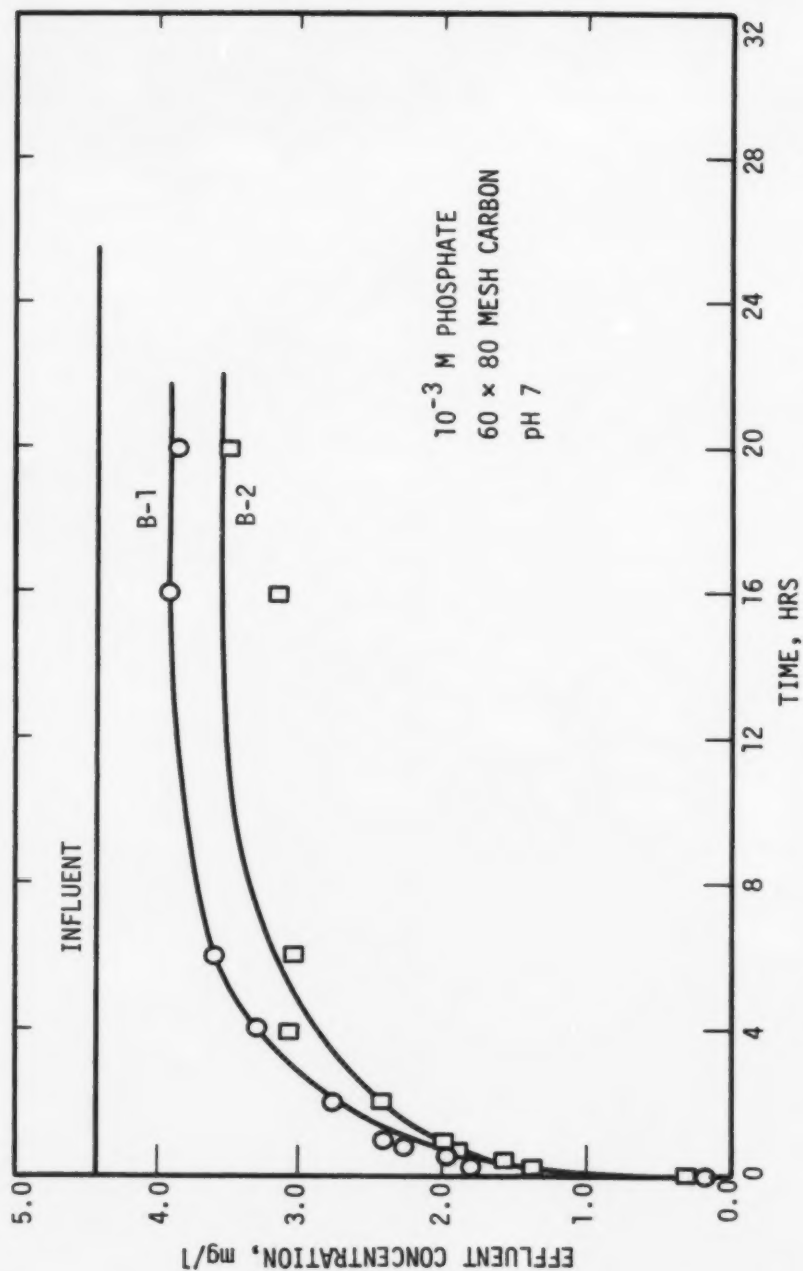


Figure 12. Commercial humic acid column runs for Carbons B-1 and B-2.

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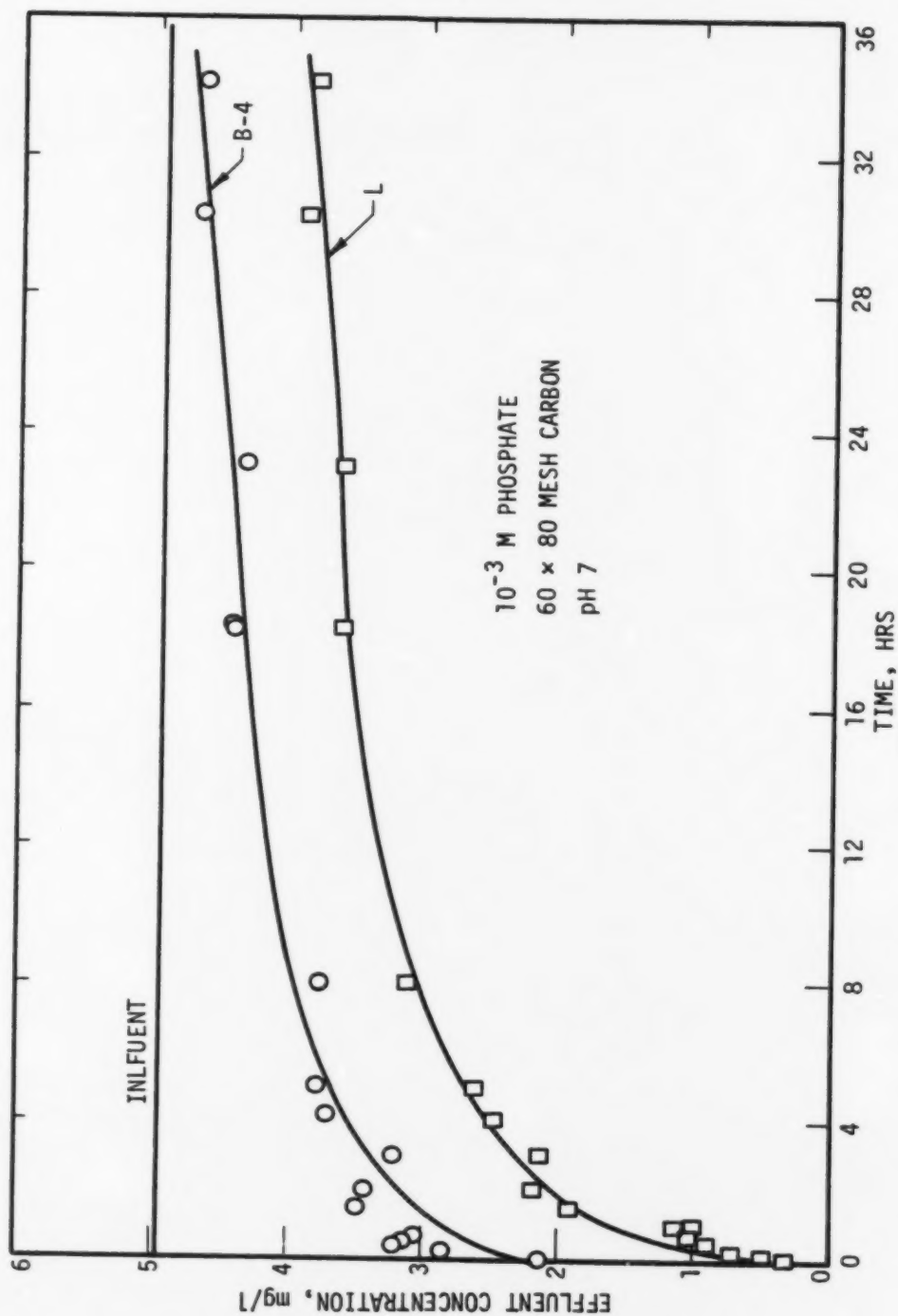


Figure 13. Commercial humic acid column runs for Carbons B-4 and L.

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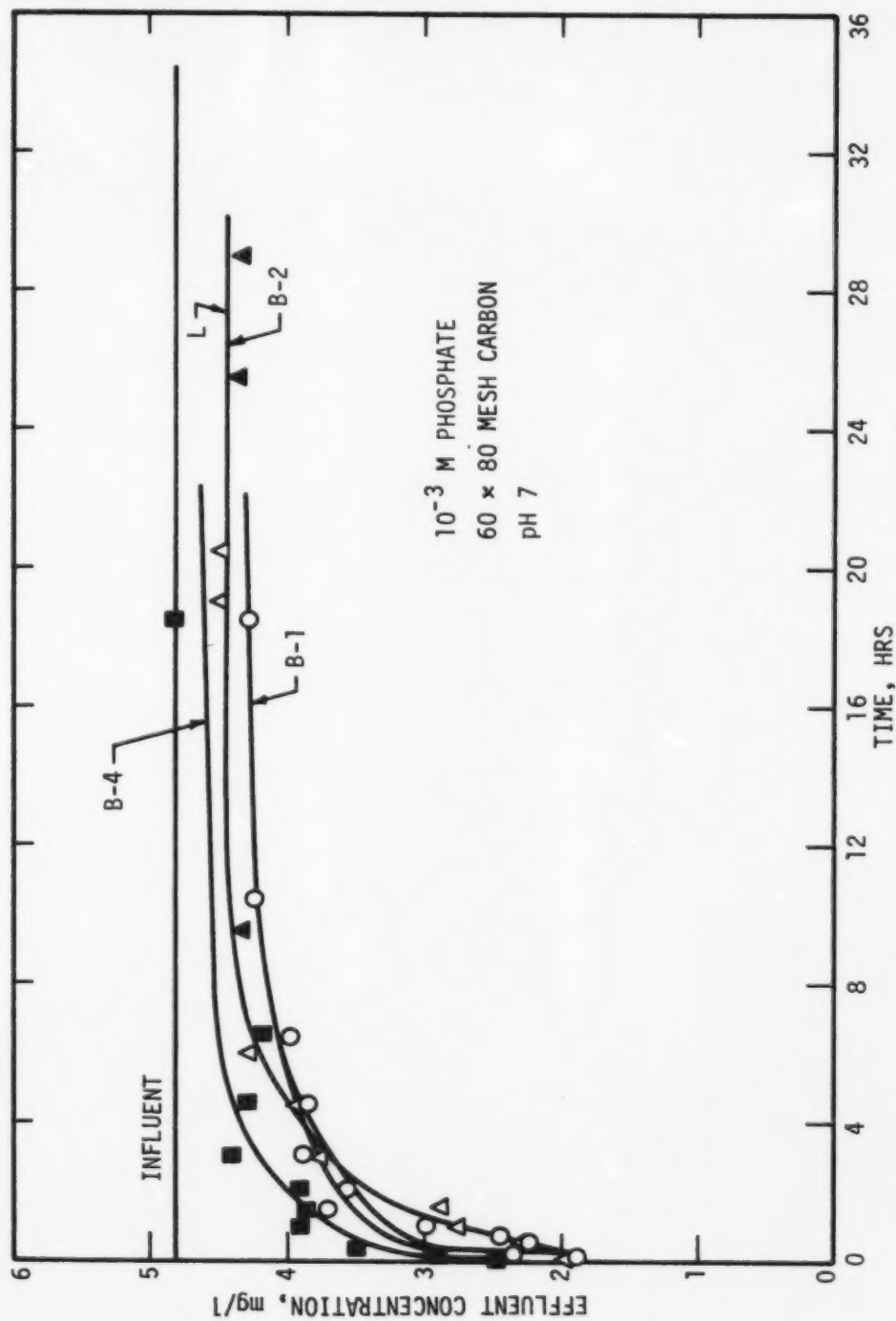


Figure 14. Leaf fulvic acid column runs.

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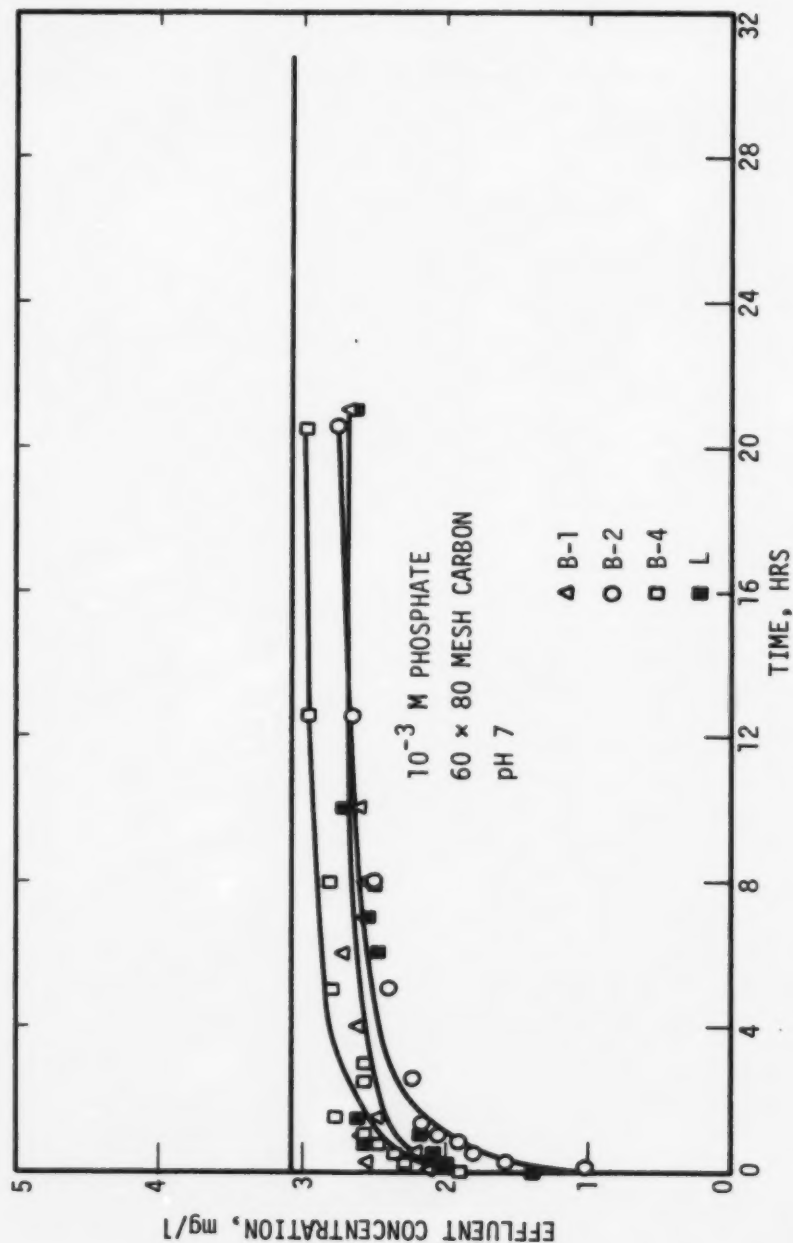


Figure 15. Soil fulvic acid column runs.

and regenerated carbon may perform differently. For a complete comparison of carbons, further studies should be conducted with the regenerated carbons. The low-activity bituminous carbons definitely performed more poorly than did the high-activity carbons. Of the resins examined, the only resin with a reasonable capacity for humic substances is the weak base phenol-formaldehyde resin. The dependence of its adsorption capacity on pH may limit its application in water treatment for removal of trihalomethane precursors, however. The styrene divinylbenzene resin, R-2, the acrylic resin, R-3, and the carbonaceous resin, CR, all had very low capacities for humic substances. Their use for removing these materials is not recommended. Further, we can conclude that the adsorption isotherms give us a reasonably good indication of the relative adsorption efficiencies of the various carbons in columns. Larger scale tests are needed, though, to determine the bed life and effluent quality that can be achieved in systems more representative of those to be used in actual practice.

## ADSORPTION OF 2-METHYLISOBORNEOL

### Adsorption Isotherms

2-Methylisoborneol (MIB) was also used to determine the relative effectiveness of carbons and resins for application in water treatment. MIB is a compound which produces earthy-musty odors and has a threshold odor limit on the order of 0.1 g/l. Detailed testing has previously been done with this compound using only one carbon as the adsorbent (Snoeyink et al., 1977; Herzing et al., 1977). Figure 16 shows MIB adsorption isotherms on carbons B-1, B-2, and L, both in deionized distilled water and in deionized distilled water initially containing 10 mg/l of humic acid. The results show carbon B-1 to have the best capacity, but carbon B-2 has a capacity very close to that of B-1. The capacity of carbon L is very low and is on the order of that obtained for the low-activity bituminous carbons B-3 and B-4. Figure 17 shows the isotherms for carbons B-3 and B-4. The ratio of the capacity on carbons B-1 or B-2 to that of L, B-3, or B-4 is approximately the same as the ratio of the surface areas, indicating that most of the surface area of each carbon is available for adsorption of MIB. The humic acid reduced the adsorption capacity of both of the bituminous based carbons but did not appear to have a significant effect on the adsorption capacity of the lignite carbon.

The MIB molecule is much smaller than that of the humic substances and these results indicate that the molecule can penetrate smaller pores and be adsorbed in them. Because the lignite carbon and the low-activity bituminous carbons have many fewer small pores they do not perform as well for a molecule of this size. Similar results are expected for other molecules of similar size and characteristics.

A study of the effect of particle size on adsorption capacity was done for carbon B-4. It was found that the capacity of 100 x 200 mesh carbon was nearly twice that of 40 x 50 mesh carbon. It should be emphasized that this finding cannot be given as a generally expected result; it is undoubtedly dependent upon the way in which the carbons were ground and their sizes were fractionated. In working with carbon sizes other than those supplied by the

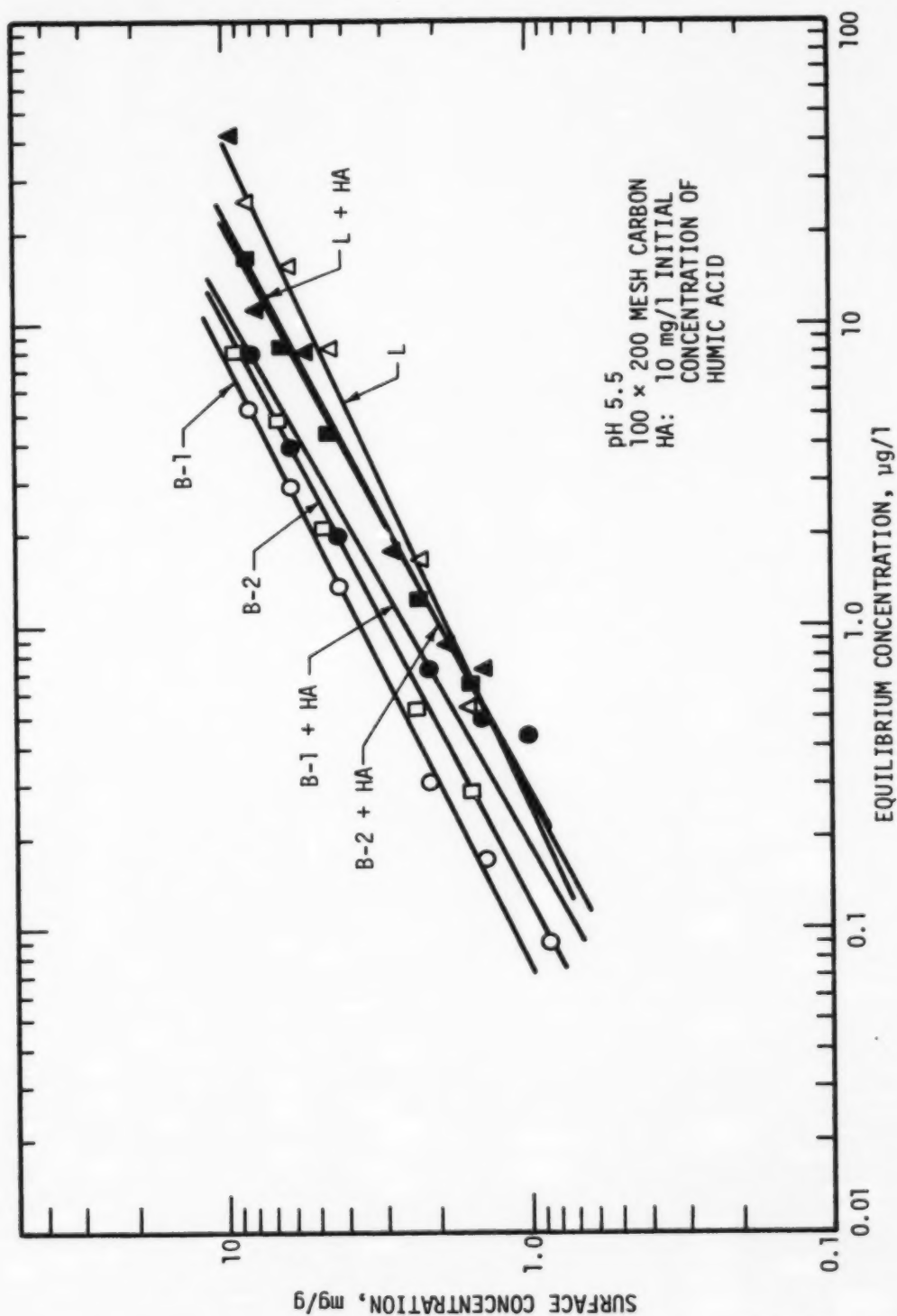


Figure 16. MIB adsorption isotherms on Carbons B-1, B-2 and L.

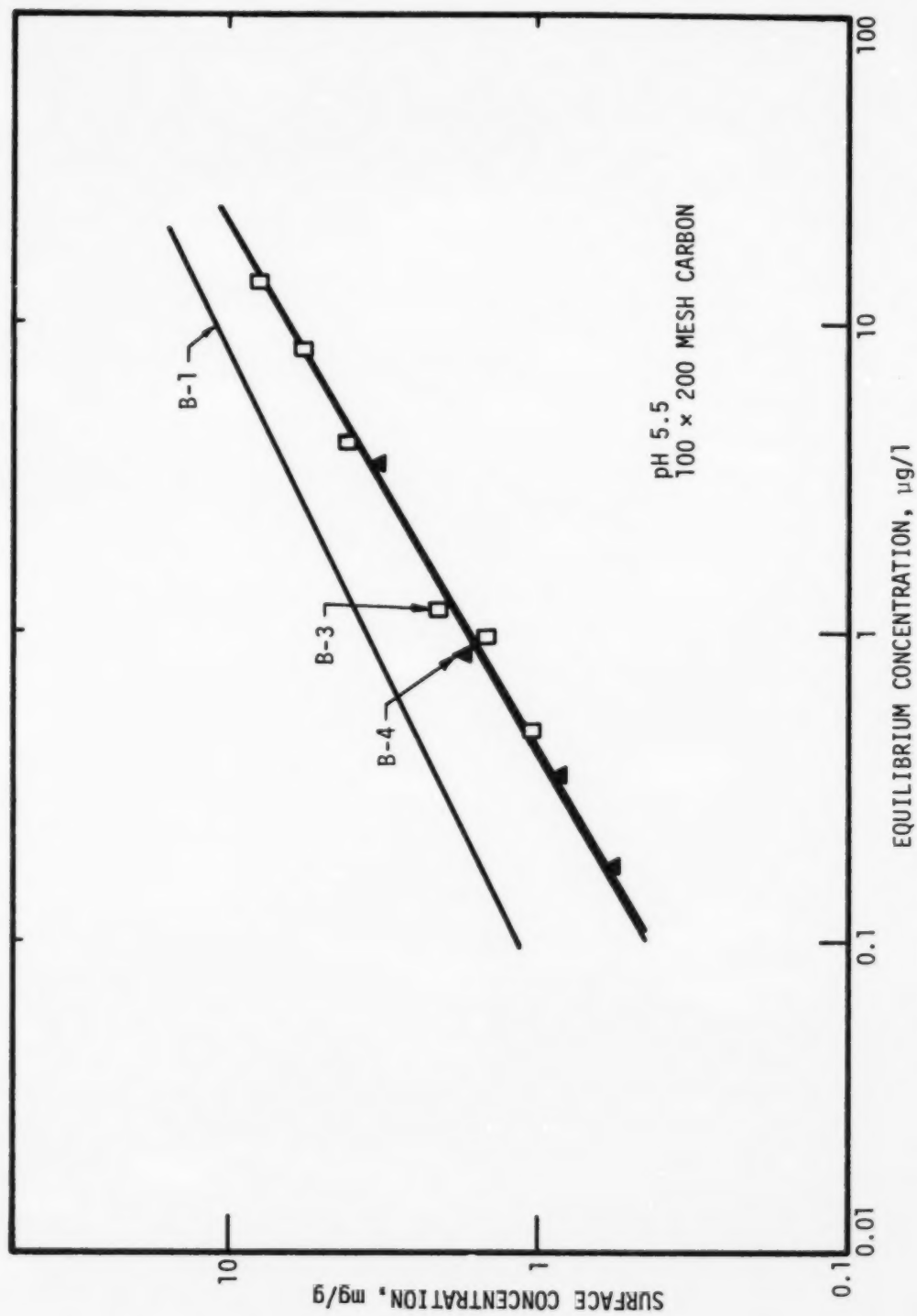


Figure 17. MIB adsorption isotherms on Carbons B-3 and B-4.

manufacturer, it is especially important to keep in mind that the activity of different particle size fractions can vary quite widely, and the extent of variation is likely to be dependent upon the type of molecule adsorbed.

Figure 18 gives adsorption isotherms for the resins R-1a, R-2, and CR, in comparison with the high-activity bituminous carbon B-1 as reproduced from Figure 16. Resin R-1a has essentially no capacity for MIB. The carbonaceous resin CR and resin R-2 did adsorb MIB, but their capacities were significantly lower than that of the high-activity bituminous carbon. One hundred mg/l of alkalinity as  $\text{CaCO}_3$  was included in the test solutions for the resin isotherms but other studies showed that this alkalinity had no effect on adsorption capacity. The presence of the humic acids appeared to have very little effect on the adsorption capacity of R-2 and CR, consistent with the observation that these two materials did not adsorb any significant amount of commercial humic acid. Based on these results, if the resins CR and R-2 are easily regenerated, it may be possible to use the resins for MIB adsorption in place of activated carbon.

An additional interesting observation was made during the MIB adsorption tests. On one occasion the resin R-2 was used without prior cleanup, just as supplied by the manufacturer. The capacity of the uncleaned resin was lower by a factor of 2 to 3 than the capacity of the clean resin, indicating that the cleaning process makes many adsorption sites available for subsequent MIB adsorption. This difference was not observed when column runs were made to compare conditioned and unconditioned R-2, however. Apparently, the impurities that interfered in the batch tests were washed out and thus did not cause a problem in the column runs. Certainly, if this resin were to be applied in water treatment processes, it would not have to be cleaned up to the same extent that it was in preparing it for our studies. Some washing would probably be necessary, though, to keep the impurities from entering the product water.

#### Column Adsorption and Resin Regeneration Tests

Small-scale columns were also run with carbons B-1 and L to determine whether the relative efficiencies as predicted from the isotherms would also hold in a column. These columns contained 2 grams of carbon each in a bed of approximately 1.3 cm diameter. Examination of Figure 19 shows that carbon B-1 performed significantly better than carbon L as is predicted on the basis of the isotherms. Again, it must be noted that because of the size of the column and the flowrate used, these columns cannot be used directly to determine how long a full-scale bed might last in actual practice. In order to obtain a good prediction, a pilot-scale study is needed. If small-scale studies are used, correlations are needed to connect them to pilot-scale and full-scale studies.

We were very interested in determining whether the MIB could be removed from the resins by applicable regeneration techniques, and columns of resin were saturated for this purpose. Figures 20 and 21 show representative breakthrough curves for MIB adsorption by resins R-2 and CR, respectively. No direct comparison can be made between these two curves because different particle sizes of the two materials were used.

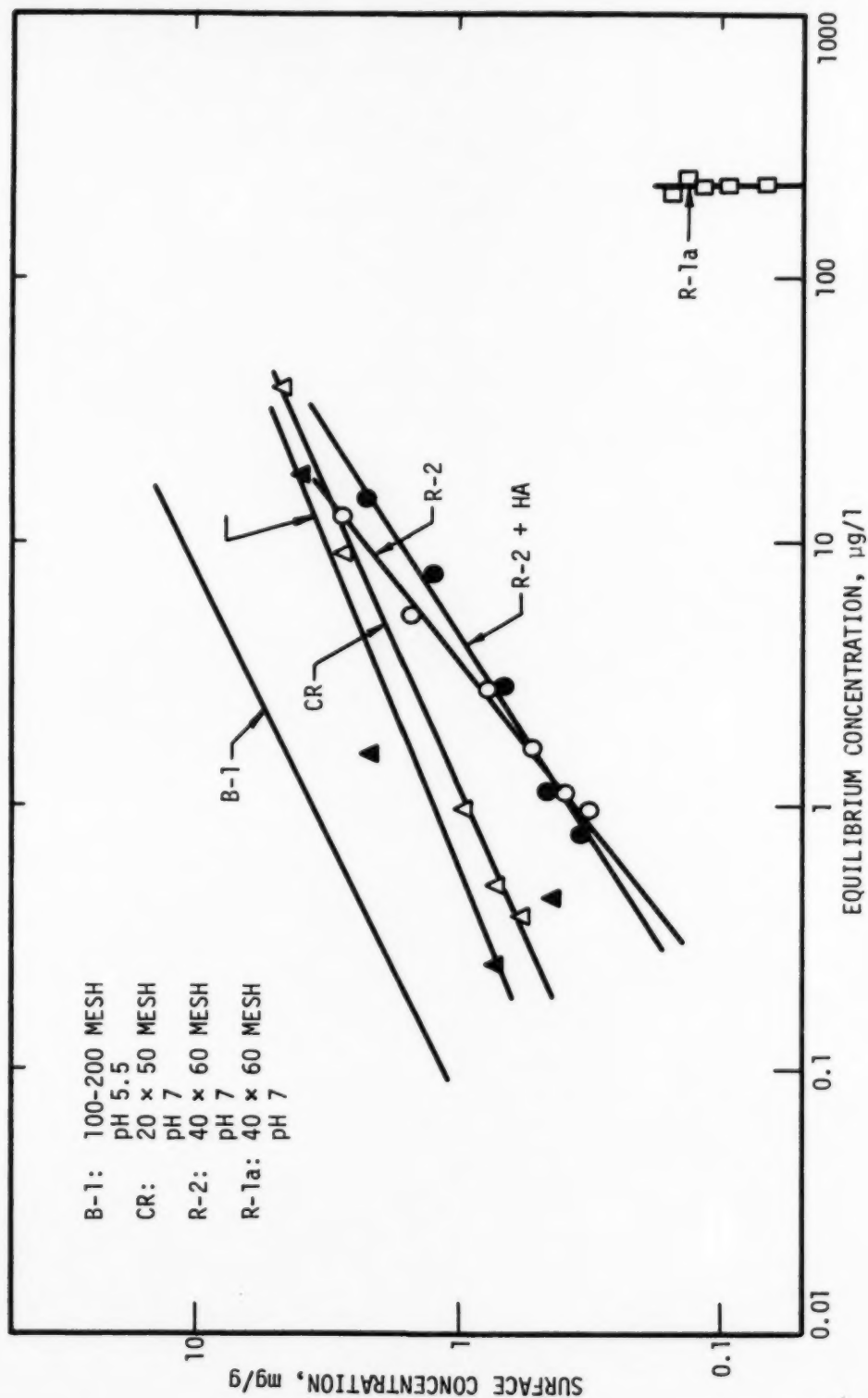


Figure 18. MIB adsorption isotherms on Resins R-1a, R-2 and CR.

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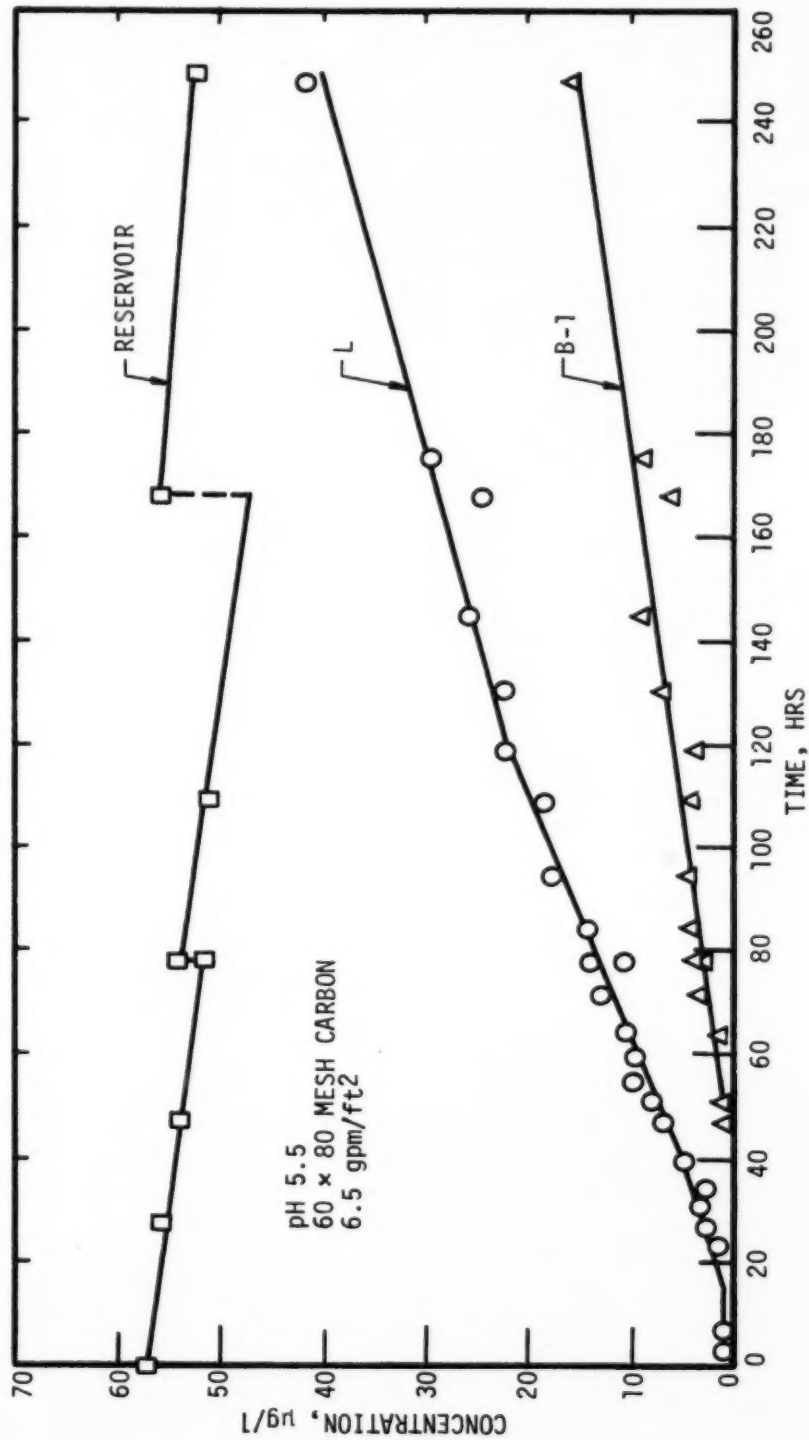


Figure 19. MIB adsorption by columns of Carbons B-1 and L.

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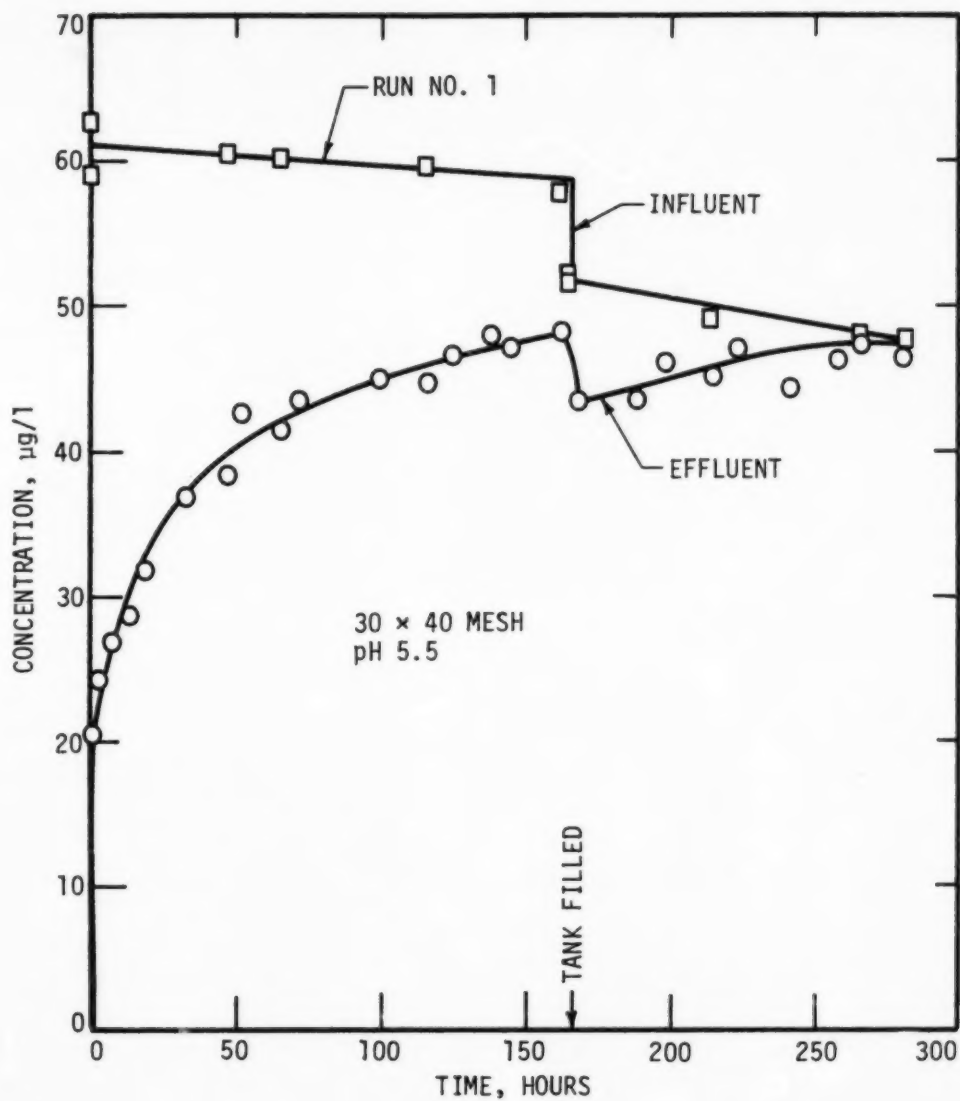


Figure 20. MIB adsorption by a column of Resin R-2.

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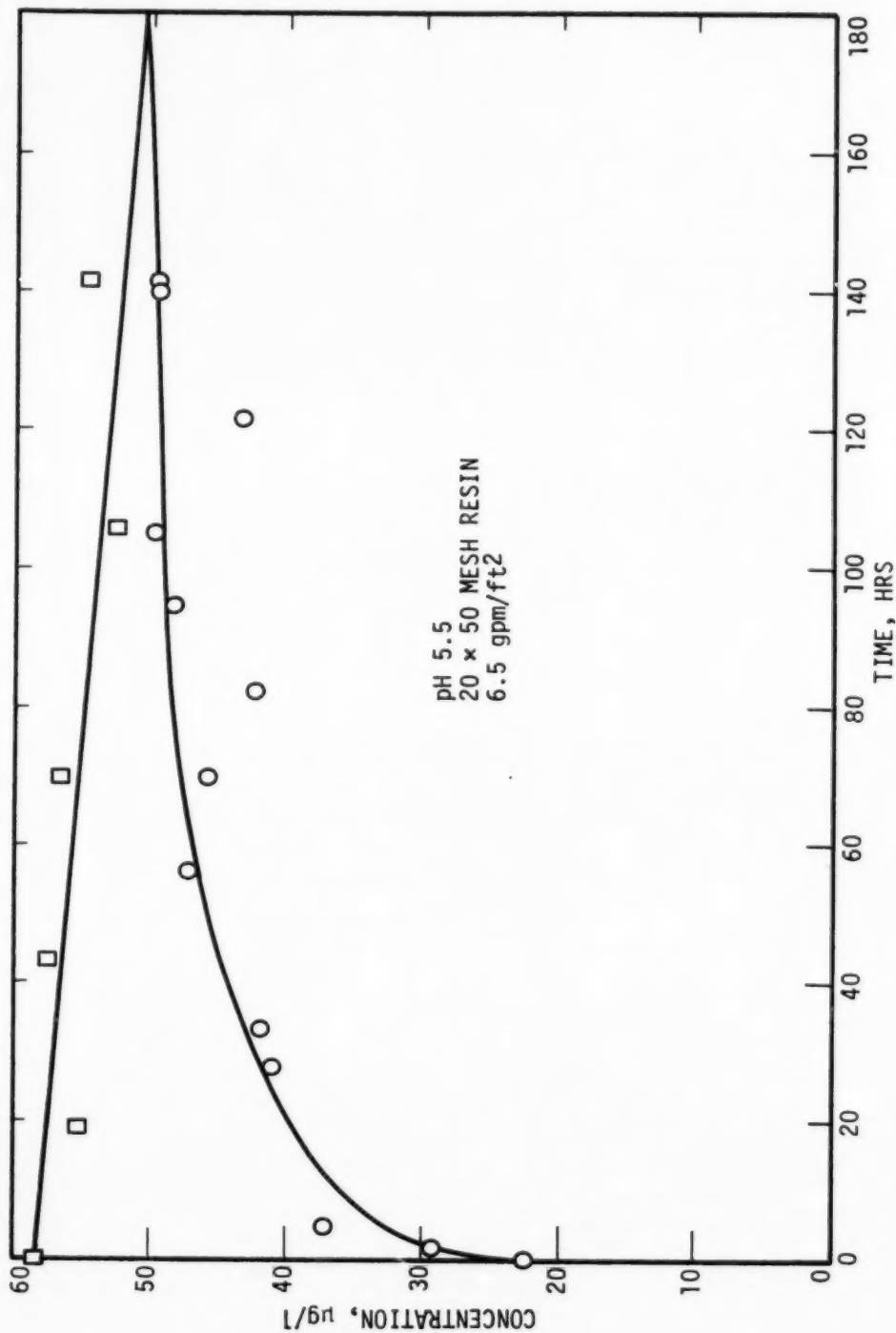


Figure 21. MIB adsorption by a column of Resin CR.

The regeneration techniques examined used steam and ethanol. It has previously been demonstrated by Slejko and Neely (1976) that chloroform could be removed from the carbonaceous resin by steam regeneration. Accordingly, we were interested in determining whether steam could also remove MIB. Ethanol was considered to be potentially applicable because MIB is quite soluble in ethanol and should desorb into it quite readily. If ethanol is used, there is also the potential for recovering it by distillation. Other nonaqueous solvents were not considered because of possible toxicity problems.

Our results with both regenerants were less than satisfactory, however. As shown in Table 3, only 5 percent of the adsorbed MIB could be recovered from the resin CR using steam. After further extraction of this resin with ethanol the bed was resaturated with MIB and again extracted with 5 bed volumes of ethanol. A recovery of only 20 percent of the amount adsorbed during the second saturation cycle was achieved.

TABLE 3. REGENERATION OF MIB SATURATED RESINS R-2 AND CR WITH STEAM AND ETHANOL

| Material  | Column/Run | Percent Recovered                      |                                  | Total |
|-----------|------------|----------------------------------------|----------------------------------|-------|
|           |            | Steam (Bed Volumes of Condensed Steam) | Ethanol (Bed Volumes of Ethanol) |       |
| Resin CR  | I/1        | 5                                      | *                                | *     |
|           | I/2        | †                                      | 20 (5 BV)                        | 20    |
| Resin R-2 | I/1        | 23 (20)                                | 53 (16)                          | 76    |
|           | I/2        | †                                      | 56 (12)                          | 56    |
|           | I/3        | †                                      | 51 (25)                          | 51    |
|           | II/1       | 34 (20)                                | 34 (16)                          | 68    |

\*Data point not obtained owing to equipment failure.

†Not determined.

Studies with the resin R-2 showed that 23 percent was initially recovered using steam and 53 percent using ethanol for a total recovery of 76 percent of that adsorbed. Subsequent saturation with MIB and regeneration of the same column with ethanol alone yielded 56 percent recovery; saturation a third time and regeneration with ethanol alone yielded 51 percent recovery. The cumulative recovery of MIB for the 3 runs was 61 percent. In a second

column of the resin R-2, approximately 34 percent of the adsorbed MIB was removed by steam (see Figure 22 for the MIB profile in the effluent during regeneration), and subsequent extraction with ethanol yielded another 34 percent for a total of approximately 68 percent recovery.

Neither of the regenerants appeared to be satisfactory alone or in combination with the other. It is possible that improved removal by the steam could be achieved if superheated steam were used. During subsequent loadings all, or nearly all, of the additional material adsorbed may be removed during the regeneration process. It should be kept in mind that whether or not some of the initial material adsorbed will be irreversibly taken up, can only be determined by running somewhat larger columns over a larger number of saturation regeneration cycles. However, the general indication is that some molecules of the type present in water supplies may not be completely removed if steam and/or ethanol is used as the regenerate, and because of this it is possible that a gradual loss of capacity will take place over time.

It is recommended that this possibility be examined at pilot-scale installations if it proves desirable to use these materials.

#### ADSORPTION OF CHLOROFORM

##### Adsorption Isotherms

Previous work by Slejko and Neely (1976) showed that the carbonaceous resin had a very high capacity for chloroform relative to other commercially available adsorbents. In their testing they compared it with several other commercially available carbons using chloroform-spiked Philadelphia tap water. They also found that atmospheric steam readily removed the adsorbed chloroform and restored the resin to essentially virgin capacity. In other work, Love (1976, personal communication) indicated that tests on Cincinnati tap water showed similar results. Accordingly, we were interested in determining the behavior of this resin relative to carbon in controlled laboratory studies in order to better explain its adsorption behavior.

Figure 23 shows chloroform isotherms for the lignite carbon, L, and the carbonaceous resin, CR, in systems containing only chloroform, and others to which commercial humic acid has been added. Examination of this figure shows the isotherm for the resin CR to be not greater than 1.5 times that for carbon L, both with and without humic substance being present. Further, the commercial humic acid had no significant effect on the adsorption capacity of either the resin or the carbon for chloroform. The absence of a competitive effect on the carbonaceous resin is consistent with the fact that many other materials are not adsorbed by it; in particular the humic acids are not adsorbed as was shown in this study. The absence of a competitive effect on the lignite carbon is somewhat surprising because this carbon has a high capacity for the commercial humic acid. It appears, however, that the commercial humic acid does not adsorb at the same sites that chloroform does and thus has no real effect on the chloroform capacity.

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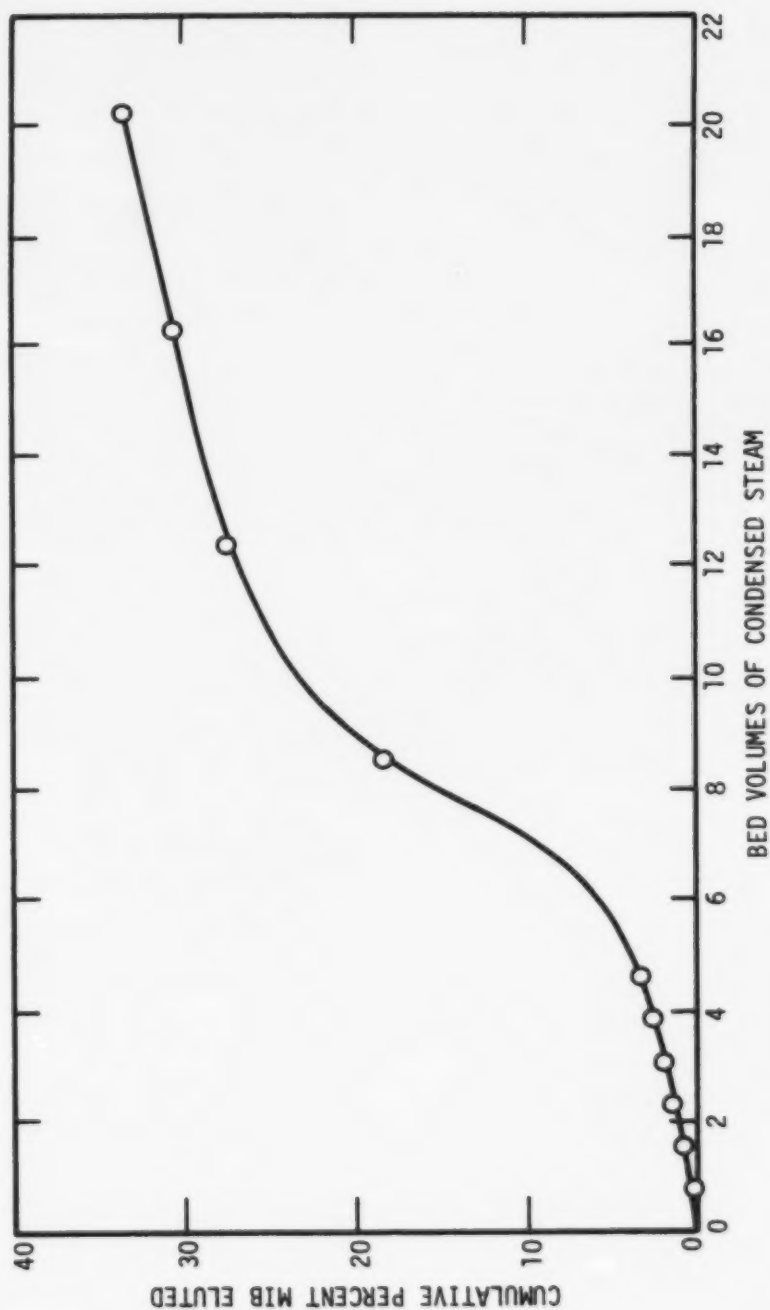


Figure 22. MIB recovery from a column of Resin R-2.

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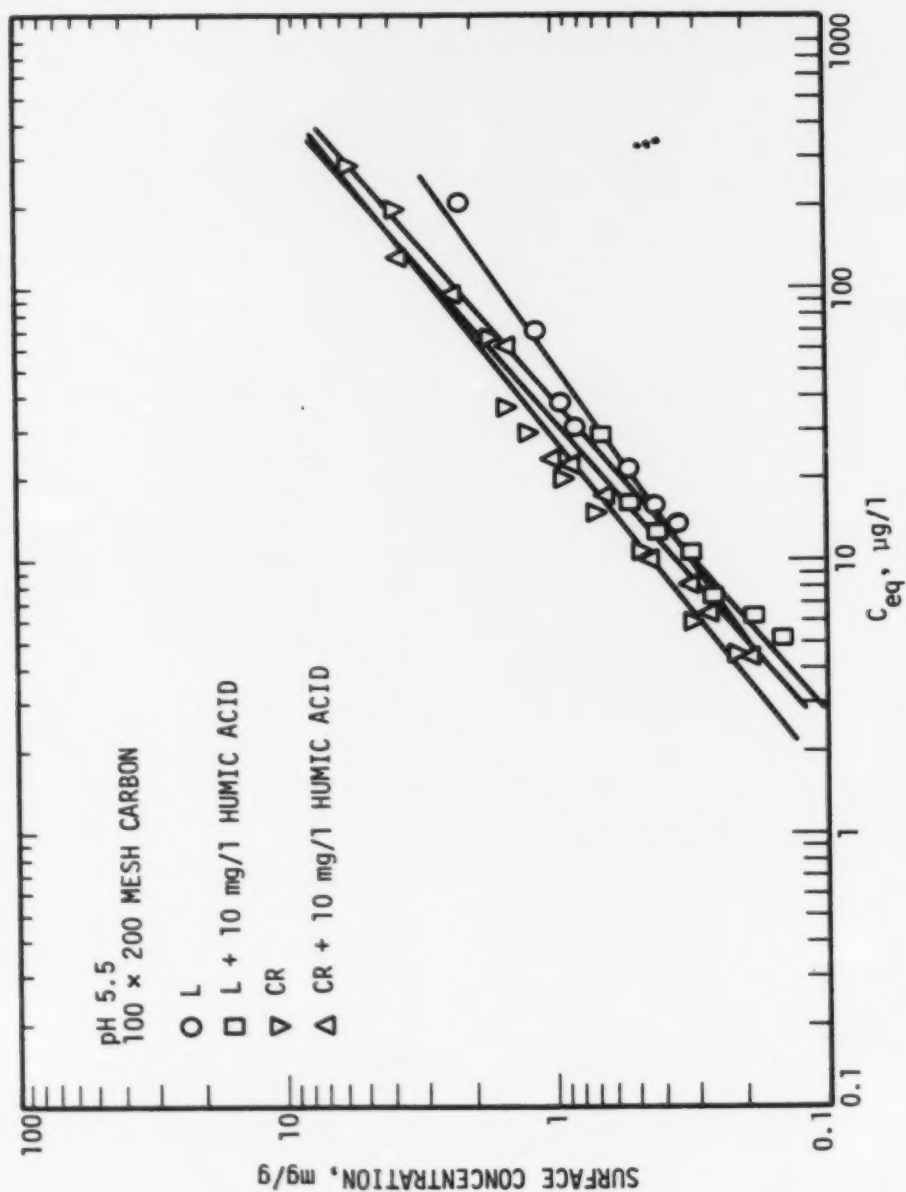


Figure 23. Chloroform adsorption isotherms on Resin CR and Carbon L.

Because the carbonaceous resin shows a capacity close to that of the lignite carbon, and the humic acid had no effect on capacity of the lignite carbon, it is reasonable to question why the significant difference in capacity was noted for the pilot-scale tests on Cincinnati tap water and Philadelphia tap water. The Slejko and Neely (1976) study was concerned only with the concentrations of chloroform greater than 1 mg/l whereas our results are for concentrations below 0.5 mg/l. This concentration range was chosen because 90 percent of the water utilities sampled by the EPA (1976b) had winter-time concentrations of less than 0.105 mg/l of chloroform in the drinking water. Thus it appears that the major application of resins for chloroform removal will be for waters with less than 0.1 mg/l. While the different concentration range may partially explain the results, a more likely explanation for the differences noted in the pilot-scale test as compared to our laboratory test is that there were organic compounds present in the tap waters of those cities which competed with chloroform on the activated carbons but not on the carbonaceous resin. Otherwise, on the basis of our study, the effectiveness of the activated carbons for chloroform removal should be comparable to that of the carbonaceous resin.

On the basis of these results it is recommended that further studies be done in different locations to compare the carbonaceous resin with commercial carbons for chloroform and other trihalomethane removal. Such studies should show whether there are some natural waters that do not contain substances that compete with chloroform for adsorption sites on activated carbon. We do not know which compounds compete or the reasons for the difference in capacities noted to date, and thus cannot predict performance without on-site tests.

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